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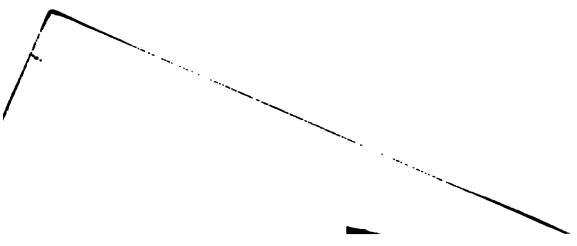

# TREATISE ON
# APPLIED ANALYTICAL CHEMISTRY

PMB
VILLAVECCHIA

# TREATISE ON APPLIED ANALYTICAL CHEMISTRY

## METHODS AND STANDARDS for the Chemical Analysis of the principal Industrial and Food Products

By

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## TRANSLATOR'S NOTE

In the preparation of the present translation, the points on which it has been considered desirable to depart from the sense of the Italian text are few and mostly unimportant. Notification is made where any appreciable addition to or modification of the original has been made to bring it into conformity with the conditions in this country.

Temperatures are always expressed in degrees Centigrade, and concentrations of aqueous alcohol solutions, according to the French custom, in percentages by volume.

THOMAS H. POPE.

BIRMINGHAM.

# PREFACE

Chemical analysis applied to the examination of industrial and alimentary products plays an important part in the purchase of raw materials, in the control of manufacturing processes, and in the determination of the value, impurities and adulterations of the finished products. It constitutes, indeed, a branch of chemistry worthy of assiduous cultivation by the technical chemist who wishes to obtain a rational knowledge of his prime materials and finished products, by the hygienic chemist desirous of detecting any additions to or changes in food substances, by the commercial chemist for the exact characterization and evaluation of commercial products, and, in general, by experts and inspectors appointed to exact contractual conditions in connexion with the purchases and supplies of the State.

The methods followed in these industrial and commercial analyses are applications of general, analytical and physical chemistry to special cases; in some instances they are less rigorous than, and do not attain the precision of, scientific methods, whereas in others the accuracy is that of the most exact scientific investigations. The choice of the method to be used is of considerable importance in practice, which demands processes giving the greatest exactitude compatible with the end in view at the lowest possible expenditure of time and trouble.

In most cases numerous methods are given in the literature for the examination of any particular material, and doubt is often felt as to which of these methods it is preferable to employ, the more so since the differences frequently lie in details and are not of great import. Thus, without preliminary trial, the analyst, especially in a new field, cannot always decide easily which procedure will answer his purpose.

It may, further, be pointed out that, with certain products, the methods of analysis at present available yield results which are not absolute but relative only to the procedure employed. In such cases it is most important that different workers use one and the same method—although perhaps not a very accurate one—in order that the results obtained may exhibit the necessary concordance. Then, too, certain States have felt the necessity of issuing official standards to be attained in the analysis of various commodities of general interest, while in commercial and industrial circles the custom is growing of fixing beforehand the analytical methods serving as basis for the evaluation of the products to be dealt in.

All this shows how useful it is for the analyst to have at his command a collection of such methods and standards for industrial and commercial analyses as, having been either officially prescribed or repeatedly tested, may be confidently adopted.

To this end the results obtained over a long period in the Chemical

Laboratories of the Italian Customs Department were embodied in a *Manual of Technological Analytical Chemistry*, which was published in 1904 and has been out of print for some years.

With a similar object the present treatise has been compiled. Much still remains to be done, and the methods now described cannot be regarded as final; in the present state of knowledge they do, however, satisfy practical requirements with some degree of sufficiency. In the laboratories under my direction, most of the methods have been repeatedly tried and many of them carried out and studied almost daily by specialists who are already well known from their published work and are now assisting here with their valuable co-operation. To these and also to those colleagues and friends who have furnished unpublished analytical data and particulars of methods based on their practical experience, I desire to express my gratitude.

This treatise is divided into two volumes. The first deals with the analysis of potable waters, chemical products, fertilizers, cement materials, metals and alloys, fuels, tar and its derivatives, mineral oils and fatty substances and the industrial products derived therefrom. The second treats of flesh foods, milk products, flour and starches, sugars and saccharine products, beer, wine, spirits and liqueurs, essential oils, turpentine, varnishes, rubber, tanning materials, leather, colouring matters, and textile fibres and fabrics.

For each product considered a brief statement is first made of the different cases and the analytical problems commonly presenting themselves, as well as of the investigations and determinations to be made to solve them. Detailed descriptions are then given of the methods to be followed. Sometimes methods for groups of allied substances, to which they are applicable in general, are collected in one and the same sub-chapter. As a rule but one method or at most two methods are given for each separate test or determination; when it is deemed necessary to give a greater number, the reason for this is stated, and the cases indicated in which one method rather than the others should be followed.

In some instances mention is made of details to be observed in special cases or of doubts which exist as to the accuracy of the methods, any factors and conditions influencing the results being pointed out. Whether the methods have been adopted by official or other bodies is also stated.

Next are given criteria and standards, with the aid of which the industrial, commercial or hygienic value of the product may be ascertained from the analytical data obtained. For the same purpose tables are given containing examples of the analytical results relating to the ordinary commercial qualities of the product.

It is my hope that this publication may be received cordially by Italian chemists, to whom I shall be grateful for suggestions of improvements or additions.

G. VITTORIO VILLAVECCHIA.

ROME.

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# CHAPTER I

# WATERS

## POTABLE WATERS

In order to judge of the potability of a water, a partial or complete analysis is made according to circumstances.

The former includes qualitative tests for ammonia, nitrates and phosphates, and determinations of the fixed residue, hardness and organic matter. Complete analysis requires, in addition, determinations of the dissolved gases and of the various mineral components (chlorine, sulphuric acid, silica, lime, magnesia, alkalies, etc.).

In either case great importance attaches to the taking of the sample and the observation of the physical characters of the water.

**Taking of the Sample.**—The sample should be collected in a new bottle of colourless glass with a ground stopper. This is washed first with pure hydrochloric acid, then repeatedly with ordinary water (the bottle being completely filled twice), and lastly with distilled water, and, when the sample is taken, it is well rinsed with the water to be analysed. Corks may be used, but these should be new and either well washed with the particular water or, better, waxed. Coloured glass bottles, especially after use, are to be excluded absolutely, as also are earthenware or metallic vessels.

To take a sample from a spring, river, reservoir, or well, the vessel should, where possible, be immersed in the water, care being taken not to collect the surface layer or the deposit at the bottom.

Where another vessel is used to transfer the water to the bottle, it must be thoroughly cleaned and then rinsed with the water itself.

Before taking a sample from a tap or pump the water in the pump or in the tube of the tap must be run away.

In the case of a spring, the surroundings must be examined—the nature of the soil and especially any cultivated ground, habitations, cemeteries, or other possible source of contamination which may be near.

With rivers the distance from the source and the course (whether through inhabited or industrial districts, etc.) are noted, together with the geological character of the ground.

In the case of wells or reservoirs, observations are made on their depth, the kind of wall, the nature of the sub-soil, and the distance from sewers or other source of contamination.

For partial analysis, 3–4 litres of water are sufficient, whilst complete analysis requires about 20 litres.

Samples should be kept in a cold, dark place and be analysed as soon as possible.

**Physical Characters.**—The colour, clearness, odour and taste are noted.

When the sample is taken, its temperature and that of the surrounding air are observed. The reaction towards litmus is also tested.

If the water is turbid, it is left at rest until clear and then filtered through a dry filter, the analysis being carried out on the filtrate. If the insoluble residue is appreciable in amount, it is weighed on a tared filter and its nature investigated.

## 1. Partial Analysis

The partial analysis of a potable water includes, besides observation of the above physical characters, the following estimations.

**1. Fixed Residue.**—In a platinum dish or crucible 200 c.c., or more if the proportion of mineral matter is low, of the water are evaporated to dryness on a water-bath or air-bath. The residue is dried in an oven, first at 100–105° to constant weight, and then at 180° to constant weight.

The residue dried at 180° is then heated to dull redness over a naked flame to see if it blackens or emits an odour of burning organic matter. When marked blackening is observed, the calcination is continued until all the carbon is burnt, the residue being then moistened with ammonium carbonate solution, calcined again at a dull red heat and reweighed. The difference in weight between the residue dried at 180° and that heated to dull redness gives approximately the quantity of non-volatile organic matter in the water.

As a rule, the residue dried at 180° is expressed in grams per 100 litres of the water.

**2. Hardness.**—A water is said to be *hard* when it dissolves soap badly and does not cook vegetables well, these being properties dependent essentially on the calcium and magnesium salts contained in the water; the degree of hardness thus represents the whole of the calcium and magnesium salts calculated as either calcium carbonate or oxide. *Total hardness* is that due to all the calcium and magnesium salts dissolved in the water; *permanent hardness*, that due to such of these salts as remain in solution after the water is boiled; *temporary hardness*, that due to those salts which are precipitated from the water on boiling, that is, which were originally dissolved as bicarbonates.

The two following methods are commonly employed for the estimation of hardness:

(*a*) Boutron and Boudet's Method.

This requires:

(1) A solution of pure calcium chloride containing 0·25 gram $CaCl_2$ per litre.[1]

(2) Soap solution, prepared by dissolving in the hot 50 grams of white

[1] This may be prepared by dissolving 0·2253 gram of pure calcium carbonate in hydrochloric acid and evaporating repeatedly to dryness to expel the excess of acid.

Castile soap in 800 grams of 90% alcohol, filtering and adding half a litre of distilled water to the filtrate.

(3) Burette containing about 5 c.c., the volume occupied by 2·4 c.c. being divided into twenty-two equal parts, each representing one degree of hardness; above the zero is another mark up to which the burette must be filled with soap solution and which represents the small quantity of the liquid necessary in each case to produce froth, but not taken account of in the calculation.

(4) Bottle with a ground-in stopper and marks indicating the volumes, 10, 20, 30 and 40 c.c.

The titre of the soap solution is first ascertained: into the bottle are poured 40 c.c. of the calcium chloride solution and into this the soap solution is gradually dropped from the burette (filled to the division above the zero point); at intervals the bottle is closed and vigorously shaken up and down. When such shaking produces a froth 5–6 mm. high at the surface of the liquid and this persists for at least 5 minutes, addition of the soap solution is discontinued. The soap solution is normal when the froth-production requires 22 divisions of the burette (in addition to that above the zero, which makes 23 in all). If less is required, the soap solution must be diluted with water, and if more, soap must be added.

When 40 c.c. of calcium chloride solution correspond exactly with 22 divisions of the soap solution, the *total hardness* of a water may be determined as above, 40 c.c. of the water being titrated with the soap solution until a froth persistent for 5 minutes is obtained; the number of divisions of the burette, calculating from zero, represents the number of *French degrees* of hardness. One French degree corresponds with 1 gram of $CaCO_3$ per 100 litres; thus, a water with 10 degrees of hardness contains 10 grams of calcium and magnesium salts, calculated as calcium carbonate, per 100 litres.

If the soap clots during the test, the water probably contains more than 30 degrees of hardness. In such case, the estimation is repeated with 20, 10, or even 5 c.c. of the water, in fact with such a quantity that, when a persistent froth is formed, the liquid is opalescent but without clots; the volume of water used is diluted to 40 c.c. with distilled water. The dilution is, of course, allowed for in calculating the hardness.

To determine the *permanent hardness*, 100 c.c. of water are boiled in a dish or flask for 20–30 minutes and, when cold, made up to the original volume with distilled water and filtered; the hardness of the filtrate is determined as above.

The *temporary hardness* is given by the difference between the total and the permanent hardness.

(*b*) CLARK'S METHOD, modified by Faisst and Knauss.

This requires:

(1) An ordinary 50 c.c. burette.

(2) A bottle holding about 200 c.c. with a ground stopper and marked at 100 c.c.

(3) A solution of crystallised barium chloride containing 0·523 gram of $BaCl_2, 2H_2O$ per litre.

(4) Soap solution: 150 grams of ordinary lead soap and 40 grams of pure dry potassium carbonate are triturated in a mortar until homogeneous and then exhausted with 96% alcohol. The filtered alcoholic solution is distilled to eliminate the solvent and of the residual soap, dried on a steam-bath, 20 parts are dissolved in 1000 parts of 56% alcohol. The soap solution thus obtained is then titrated as follows. One hundred c.c. of the barium chloride solution are introduced into the bottle, the soap solution being then run in gradually from the burette and the bottle closed and shaken from time to time until a froth 5–6 mm. high, persistent for 5 minutes, is formed. The soap solution is then either diluted with 56% alcohol or concentrated by addition of soap until exactly 45 c.c. correspond with 100 c.c. of the barium chloride solution.

The hardness of a water is determined similarly, 100 c.c. of the water being taken, or, with very hard waters which produce clots, 50, 20 or 10 c.c., or, in general, such volume as requires from 20 to 45 c.c. of the soap solution; this volume is made up to 100 c.c. with distilled water before titration.[1] The result obtained is then corrected for the dilution.

If the water is very rich in magnesium salts, it is well to wait a few minutes after each addition of soap solution and before shaking in order that all the magnesium may combine with the soap.

From the number of degrees of soap solution necessary to produce a persistent froth with 100 c.c. of the water the hardness in *German degrees* is calculated by means of Table I. One German degree represents 1 gram

TABLE I

*Clark's Hardness Table, compiled by Faisst and Knauss.*

| Soap Solution used in c.c. | Corresponding degrees of hardness. | Number of degrees corresponding with 1 c.c. of soap solution. | Soap Solution used in c.c. | Corresponding degrees of hardness. | Number of degrees corresponding with 1 c.c. of soap solution. |
|---|---|---|---|---|---|
| 3·4 | 0·5 | | 26·2 | 6·5 | |
| 5·4 | 1·0 | 0·250 | 28·0 | 7·0 | 0·277 |
| 7·4 | 1·5 | | 29·8 | 7·5 | |
| 9·4 | 2·0 | | 31·6 | 8·0 | |
| 11·3 | 2·5 | | 33·3 | 8·5 | |
| 13·2 | 3·0 | | 35·0 | 9·0 | |
| 15·1 | 3·5 | 0.260 | 36·7 | 9·5 | 0·294 |
| 17·0 | 4·0 | | 38·4 | 10·0 | |
| 18·9 | 4·5 | | 40·1 | 10·5 | |
| 20·8 | 5·0 | | 41·8 | 11·0 | |
| 22·6 | 5·5 | 0·277 | 43·4 | 11·5 | 0·310 |
| 24·4 | 6·0 | | 45·0 | 12·0 | |

[1] To judge of the quantity of water to be taken, a preliminary test is made by shaking in a test tube 20 c.c. of the water with 6 c.c. of the soap solution. If the liquid becomes opalescent, 100 c.c. of the water may be taken; if it becomes very turbid, 50 c.c., or, if it gives a precipitate, 20 or 10 c.c. according to the amount of the precipitate.

of CaO per 100 litres of water, so that a water with 10 German or Clark degrees will contain 10 grams per 100 litres of calcium or magnesium oxide combined with carbonic, sulphuric, hydrochloric and nitric acids.[1]

If the number of c.c. of soap solution used does not occur in the table, the corresponding degree of hardness is determined by interpolation.

Examples. 100 c.c. of a water required 39·8 c.c. of soap solution ; the nearest number in the table is 40·1, corresponding with 10·5 degrees of hardness. Hence

$$40{\cdot}1 - 39{\cdot}8 = 0{\cdot}3$$
$$0{\cdot}3 \times 0{\cdot}294 = 0{\cdot}0882$$
$$\text{and } 10{\cdot}5 - 0{\cdot}0882 = 10{\cdot}4118,$$

the degree of hardness being therefore 10·41.

Another water required 32·0 c.c. of soap solution ;

$$32{\cdot}0 - 31{\cdot}6 = 0{\cdot}4$$
$$0{\cdot}4 \times 0{\cdot}277 = 0{\cdot}1108$$
$$\text{and } 8{\cdot}0 + 0{\cdot}1108 = 8{\cdot}11$$

The permanent and also the temporary hardness are determined as under (*a*).

The relations between French, English, and German degrees of hardness are shown in the following table :

| | French degrees. | German degrees. | English degrees. |
|---|---|---|---|
| 1 French degree . . . . | 1 | 0·56 | 0·70 |
| 1 German degree . . . . | 1·79 | 1 | 1·25 |
| 1 English degree . . . . | 1·43 | 0·80 | 1 |

**3. Alkalinity.**—By the *alkalinity* of a water is meant the quantity of calcium and magnesium carbonates and, where present, alkali carbonates present in the water ; it is, therefore, related to the hardness.

Its determination, proposed by Wartha and Pfeiffer, may replace that of the hardness, especially when it is desired to compare rapidly a number of samples of water or to detect any slight variations which a given water may undergo.

According to Gigli, the alkalinity of a water (total, permanent and temporary) is easily determined as follows : [2]

100 c.c. of the water are titrated with N/20-hydrochloric acid in presence of 2 drops of 0·1% aqueous methyl orange solution. The result is expressed as $CaCO_3$ per litre (1 c.c. = 0·0025 gram of $CaCO_3$) and represents the *total alkalinity*, that is, the alkali and alkaline earth carbonates.

Another 100 c.c. of the water is boiled for 12 minutes in a reflux apparatus, allowed to cool and filtered, the filter being washed with a little boiled, distilled water and the whole of the filtrate titrated as before. From the volume of N/20-acid used in this second determination it is necessary to subtract that required to neutralise the alkalinity transferred to the water from the glass during boiling, this being determined by a blank test with distilled water. Good Jena glass produces in 100 c.c. of water, after 12 minutes' boiling, an alkalinity corresponding with about 0·25 c.c. of N/20-HCl.

[1] ***English degrees*** represent grains of CaO per gallon of water, that is grams of CaO per 70 litres.

[2] ***L'industria chimica, mineraria e metallurgica***, 1914, p. 289.

The result, expressed as $CaCO_3$ per litre, represents the *permanent alkalinity* (due to magnesium carbonate and alkali carbonates).

Finally, the difference between the two above alkalinities represents the *temporary alkalinity*, that is, the calcium existing as bicarbonate, which is precipitated as carbonate during boiling.

**4. Ammonia.**—This is determined by means of *Nessler's solution* prepared by dissolving 50 grams of potassium iodide in 50 c.c. of hot water and gradually pouring into this solution concentrated mercuric chloride solution until the red precipitate begins to refuse to redissolve (20–25 grams of mercuric chloride are required). To the filtered liquid is added a solution of 150 grams of potassium hydroxide in 150 c.c. of water, the total volume being made up to a litre with distilled water; 5 c.c. of the concentrated mercuric chloride solution are then added and the liquid shaken and allowed to stand, the clear liquid being decanted into a bottle which is kept tightly stoppered with a rubber bung and in the dark.

One hundred c.c. of the water are poured into a glass cylinder with a ground stopper and 0·5 c.c. of sodium hydroxide solution (1 : 2) and 1 c.c. of sodium carbonate solution (2·7 : 5) added. The liquid is shaken and then allowed to stand, the clear liquid being decanted from the deposited precipitate into another glass cylinder and treated with 1–2 c.c. of Nessler reagent. The formation of a reddish-yellow turbidity or precipitate indicates that the water contains ammonia, the amount of the latter increasing with the intensity of the turbidity or precipitation.[1]

**5. Nitrous Acid (Nitrites).**—Nitrites are detected by *Griess's reagent*, comprising: (1) saturated $\alpha$-naphthylamine hydrochloride solution, (2) saturated sulphanilic acid solution, and (3) 10% pure hydrochloric or sulphuric acid solution.

From 10 to 50 c.c. of the water are introduced into a glass cylinder with a ground stopper, 3 drops of the sulphanilic acid solution, 1 drop of the hydrochloric or sulphuric acid, and 3 drops of the $\alpha$-naphthylamine hydrochloride solution being successively added. The presence of nitrite in the water is indicated by a coloration varying between rose red and deep red according to the proportion.[2]

**6. Nitric Acid (Nitrates).**—The qualitative test for nitrates may be made with the ordinary reagent consisting of ferrous sulphate and sulphuric acid, the water being used as such or after concentration to a small volume.

Traces of nitric acid may be detected by means of brucine: 2–3 c.c. of the water are treated in a porcelain dish with a crystal of brucine and a few drops of concentrated sulphuric acid free from nitric acid; the presence of nitrates in the water is shown by a red coloration rapidly changing to greenish-yellow. For the quantitative determination, see Complete Analysis (5).

**7. Phosphoric Acid (Phosphates).**—10 c.c. of the water, either as such or after concentration, are acidified with nitric acid, treated with

[1] If comparison is made with standard ammonium chloride solutions, the quantity of ammonia (or ammonium salts) in the water may be calculated.

[2] This method may similarly be rendered quantitative.

excess of ammonium molybdate solution, heated to about 40° and stirred, and examined for yellow turbidity or precipitate.

**8. Organic Matter.**—Indications of the presence of organic matter in a water are obtained from the blackening of the dry residue when heated, provided the amount present is marked. For quantitative determination, recourse is had to the indirect method of oxidising with potassium permanganate and calculating the oxygen necessary for the combustion of the organic matter.

The methods most commonly used are the following:

(*a*) KUBEL'S METHOD, which requires:

(1) Distilled water free from organic matter, obtained by redistilling water with a little permanganate.

(2) Pure dilute sulphuric acid, 1 : 3.

(3) N/100-potassium permanganate solution, containing 0·3163 gram of $KMnO_4$ per litre.

(4) N/100-oxalic acid, containing 0·63 gram of $H_2C_2O_4$, $2H_2O$ per litre.

The last two solutions should correspond volume with volume. To check this, 20 c.c. of the oxalic acid solution are heated nearly to boiling with 5 c.c. of the sulphuric acid and then titrated with the permanganate until a pink coloration persists: 20 c.c. should be required.

To 100 c.c. of the water are added 5 c.c. of the sulphuric acid and then 10 or more c.c. of the permanganate, so that the liquid remains coloured even after boiling. The liquid is boiled for 5 minutes, a volume of the oxalic acid equal to that of the permanganate taken being then added. The solution, which is then colourless, is titrated in the hot with permanganate.

The difference between the total volume of permanganate used and that necessary for the oxidation of the oxalic acid added (in other words the volume of permanganate used in the final titration) gives the volume of permanganate consumed in the oxidation of the organic matter. Since 1 c.c. of N/100-permanganate corresponds with 0·00008 gram of oxygen, the number of c.c. of permanganate consumed must be multiplied by 0·08 to obtain the grams of oxygen used up in oxidising the organic matter in 100 litres of the water. On the assumption that 1 part of permanganate oxidises very nearly 5 parts of organic matter, the amount of the latter per 100 litres of water is sometimes calculated by multiplying the number of c.c. of permanganate used up by 1·58.

(*b*) SCHULZE AND TROMMSDORFF'S METHOD. This requires the same reagents as the preceding method, together with pure sodium hydroxide solution (1 : 2).

One hundred c.c. of the water are boiled for 10–15 minutes with 0·5 c.c. of the caustic soda solution and 10 c.c. of the permanganate, allowed to cool to about 60°, mixed with 5 c.c. of the sulphuric acid and 10 c.c. of the oxalic acid solution, and titrated with the permanganate. The oxygen consumed and the organic matter present are then calculated as described under (*a*).

With either of these methods it is always necessary to make a blank

test with distilled water and to make allowance for any permanganate consumed thereby.

## 2. Complete Analysis

Complete analysis of a water includes, in addition to the determinations of the partial analysis, the following estimations.

**1. Dissolved Gases.**—The gases usually found dissolved in water are oxygen, nitrogen and carbon dioxide. They are measured by extracting them from the water by means of a pump or by boiling, collecting them in a graduated vessel and measuring their total volume. The carbon dioxide is then absorbed by caustic potash, and the oxygen by alkaline pyrogallol, the nitrogen remaining.

The apparatus and methods used for estimating gases in water are many, and detailed descriptions of them may be found in special treatises.[1] One of the simplest modes of procedure consists in using an ordinary nitrometer (Fig. 1).

The water to be examined is collected in a tared half-litre flask, *A*, which is filled completely and is then closed with a perforated rubber stopper through which passes a glass tube sealed at the lower end and furnished with a lateral orifice, the latter remaining within the stopper during transport so that the flask is kept hermetically sealed.

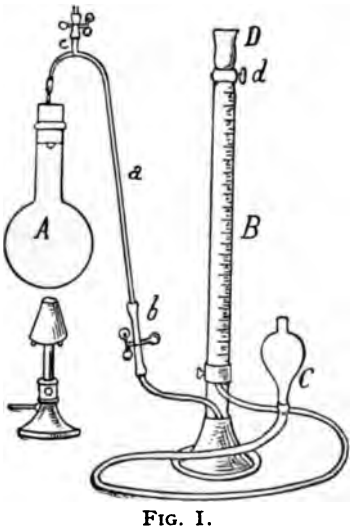

FIG. I.

The full flask is weighed to give the amount of water taken and is then arranged on a gauze over a burner and connected with the nitrometer, *B*, by means of the tube *a*. The nitrometer should be filled with previously boiled, saturated sodium chloride solution, which is also used to fill the small tube in the stopper of the flask and the whole of the tube *a*, so that no bubble of air remains in the apparatus. By means of a T-piece inserted in the tube *a* at *c*, it is easy, by opening the clips at *b* and *c* to fill the whole with the salt solution in the nitrometer.

When all is ready, the small tube is forced down until its lateral orifice is below the stopper of the flask, the clip *b* is opened and the flask heated, the liberated gases collecting in the nitrometer. During all this time the bulb, *C*, of the nitrometer is kept down. When evolution of gas ceases, the clip *b* is closed, the bulb *C* raised until the level of the liquid in it corre-

[1] For instance, Frankland, *Water Analysis* (London, 1880); Tiemann und Gaertner, *Die chemische und bakteriologische Untersuchung des Wassers*, 4th edit. (Brunswick, 1893); Ohlmüller, *Die Untersuchung und Beurteilung des Wassers und Abwassers: Leitfaden für die Praxis und zum Gebrauch im Laboratorium* (1910); Pearmain and Moor, *The Chemical and Biological Analysis of Water* (London, 1899); Lunge, *Technical Methods of Chemical Analysis* (London, 1908). Fresenius, *Quantitative Analysis*; Guareschi, *Nuova enciclopedia di chimica*, Vol. III (Turin, 1901).

sponds with that in the nitrometer tube, and the volume of gas read off, the temperature and barometric pressure being observed. The bulb *C* is then lowered and concentrated caustic potash solution introduced into the nitrometer by means of the funnel *D* and the tap *d*, care being taken to avoid entry of air. The instrument is then well shaken so that the caustic potash may absorb the carbon dioxide and the volume of the remaining gas read off after the two levels of the liquid have been brought into agreement by raising *C*. These operations are subsequently repeated after a freshly prepared concentrated solution of pyrogallol in excess of potassium hydroxide has been introduced into the nitrometer, the latter being left for about an hour after shaking in order that all the oxygen may be absorbed. The volume of the residual gas is then read with the usual precautions.

The first reading gives the total volume of the three gases, $CO_2 + N + O$, the second the volume of $N + O$ and hence, by difference, the $CO_2$, and the third the N and therefore, by difference, the O. The volumes thus obtained must be reduced to the temperature 0° and the pressure 760 mm., this being done by means of the formula,

$$V = \frac{v\ (P - p - f)}{760\ (1 + 0{\cdot}00367\ t)},$$

where $V$ is the volume of gas at 0° and 760 mm., $v$ the volume actually read off, $P$ the barometric pressure, $p$ the correction of the pressure for the temperature $t$ (found from suitable tables), $f$ the correction of the pressure for the water vapour (from tables), and $t$ the temperature. Finally the volumes of the different gases are calculated per 100 litres of the water.

**2. Carbonic Anhydride.**—As a rule, estimations are made of the total carbon dioxide, that in the free state and that semi-combined, i.e., existing as bicarbonates.

(*a*) Total Carbon Dioxide. To 0·5 or 1 litre of the water, collected so that no trace of gas escapes in a flask which is almost completely filled,[1] are added 5–10 c.c. of concentrated ammoniacal calcium chloride solution,[2] the flask being then closed tightly with a rubber stopper. After some time (24 hours or more) the water is heated on a steam-bath, access of air being avoided as far as possible; it is then filtered rapidly, the filter being kept covered with a glass. The precipitate of calcium carbonate is washed with boiled water until ammonium oxalate fails to render the wash water turbid. Any calcium carbonate adhering to the walls of the flask is dissolved in a little dilute hydrochloric acid and the solution and water used for subsequent washing out of the flask placed in a small beaker, where the calcium carbonate is reprecipitated by addition of hot sodium carbonate solution; this precipitate is filtered on the original filter and the whole washed until the wash water is no longer alkaline.

The filter with the calcium carbonate is introduced into an apparatus for the determination of carbon dioxide (*see* chapter on Cement Materials). The weight of $CO_2$ found is then referred to 100 litres of water.

[1] It is convenient to use a flask tared with its rubber stopper, and to weigh it after nearly filling it with the water; from the weight of the water the volume may be obtained by dividing by the density.

[2] This operation is best carried out where the water is collected.

(*b*) FREE AND SEMI-COMBINED CARBON DIOXIDE. To 200 c.c. of the water are added 25 c.c. of N/10-baryta solution and 2 c.c. of highly concentrated calcium chloride solution. The mixture is left for some hours in a tightly closed vessel; 100 c.c. of the liquid are then drawn off and the excess of baryta present determined with decinormal hydrochloric acid and phenolphthalein. The number of c.c. of acid used is multiplied by 2·27 since the total volume of the liquid was 227 c.c.; the product is subtracted from the number of c.c. of acid necessary to neutralise 25 c.c. of the baryta, and the difference, being equivalent to the baryta precipitated by the free and semi-combined carbon dioxide, when multiplied by 0·0022 gives the free and semi-combined carbon dioxide in 200 c.c. of the water.

**3. Chlorine** (*Volhard's method*).—To 50 or 100 c.c. of the water, acidified with nitric acid, is added more than sufficient decinormal silver nitrate solution to precipitate all the chlorine (usually 5 or 10 c.c. suffice); the liquid is shaken, allowed to settle, and filtered, both the precipitating vessel and the filter being well washed.[1] To the filtered liquid are added a few drops of ferric alum solution and a little nitric acid, the excess of silver being then determined by titration with N/10 ammonium thiocyanate solution until a pinkish-yellow coloration appears. The difference between the volume of silver nitrate taken and that of the thiocyanate required to precipitate the excess of silver, multiplied by 0·00355, gives the amount of chlorine in grams in the volume of water taken.

**4. Sulphuric Acid.**—200 c.c. or more (up to 1 litre) of the water, according as it is rich or poor in sulphates, are acidified with hydrochloric acid and evaporated to small volume (100–150 c.c.), the liquid being then treated with barium chloride, heated, allowed to deposit, and filtered; the precipitated barium sulphate is washed with water, dried, calcined (the filter paper being burned separately), and weighed: 1 part of $BaSO_4$ = 0·3433 part $SO_3$.

**5. Nitric Acid.**—One litre of the water is evaporated to a few c.c. and the nitric acid then determined by one of the ordinary methods (*see* Fertilisers: Determination of Nitric Acid).

**6. Phosphoric Acid.**—One litre or more of the water is evaporated to a small volume, in which the phosphoric acid is estimated by precipitation as ammonium phosphomolybdate (*see* Fertilisers: Determination of the total Phosphoric Acid).

**7. Silica.**—One or more litres of the water, according to the amount of the fixed residue, are evaporated to dryness in a platinum dish, the residue being dried at 105°, treated with hydrochloric acid, evaporated again and dried at 105°. It is then treated with hydrochloric acid and water and the liquid filtered, the silica being washed, dried, calcined, and weighed as $SiO_2$.

**8. Iron and Aluminium.**—The filtrate from the preceding operation is treated with a little ammonium chloride and a slight excess of ammonia and heated; if a precipitate is formed, this is filtered off, washed, dried, calcined, and weighed; it represents $Fe_2O_3 + Al_2O_3$.

[1] To save time, after the silver nitrate is added the liquid is made up to a known volume and filtered, an aliquot part being taken for the titration of the excess of silver.

**9. Lime.**—The filtrate from the preceding operation is concentrated to some extent and treated with ammonia and ammonium oxalate; the calcium oxalate formed is filtered off, washed, dried, and strongly heated in the blowpipe flame until it undergoes no further loss of weight; this represents CaO.

**10. Magnesia.**—The filtrate from the calcium oxalate is evaporated to dryness in a platinum dish and the residue gently heated to expel all the ammonium salts and then redissolved in very dilute hydrochloric acid. The solution is neutralised with ammonia solution and treated with neutral ammonium carbonate solution in such amount that the precipitate at first formed redissolves. The liquid is then left for 12 hours to allow of the complete precipitation of the magnesium as magnesium ammonium carbonate, which is filtered off, washed with dilute ammonium carbonate solution, dried, calcined, and weighed as magnesia (MgO).

**11. Alkalies.**—The filtrate from the previous operation is evaporated to dryness with ammonium chloride in a platinum dish, the residue being carefully calcined and the pure alkali chlorides remaining then weighed. If the chlorine is estimated, the amounts of $K_2O$ and $Na_2O$ present may be calculated (*see* Fertilisers: Stassfurt Salt).

**12. Poisonous and other Metals.**—The residue from the evaporation of some litres of the water may be tested for the poisonous heavy metals, such as lead, copper, barium, etc., and for elements found only in traces in potable waters, such as boron, iodine, bromine, lithium, etc.

**13. Calculation of the Analytical Results.**—As a rule the amounts of the different constituents are referred to 1 litre or 100 litres of the water, all the elements estimated being expressed as oxides with the exception of chlorine.

To check the results the amounts of the metallic oxides ($Na_2O$, CaO, MgO) and of the acid anhydrides ($SO_3$, $N_2O_5$, $SiO_2$, $CO_2$) and chlorine are added together, an amount of oxygen equivalent to the chlorine being subtracted from the sum; the remainder should be sensibly equal to the fixed residue dried at 180°.

The salts contained in the water may be reconstructed by uniting the bases and acids in their most probable combinations. The chlorine is first combined with the sodium and any excess (rare) with calcium. The sulphuric acid is united with the lime and the nitric acid with the potash and lime, or with the ammonia (if such is present). The rest of the lime, magnesia and potash is united with the carbon dioxide; the silica remains free.

If, however, the evaporated water exhibits an alkaline reaction, it contains sodium carbonate, generally together with sulphate and chloride; the lime and magnesia are then all combined with carbon dioxide.

***

A water may be said to be potable when it is clear, colourless, odourless, of pleasant taste, cool and of constant temperature and does not contain more than certain limiting proportions of various dissolved matters. According to different authors, these limits are as follows:

| | Per 100 litres. |
|---|---|
| Lime, CaO | up to 12 grams |
| Magnesia, MgO | ,, 4 ,, |
| Sulphur trioxide, $SO_3$ | ,, 0·2–10 ,, |
| Chlorine, Cl | ,, 0·2–3·5 ,, |
| Nitric anhydride, $N_2O_5$ | 0·4–2·7 ,, |
| Nitrous anhydride, $N_2O_3$ | 0 |
| Ammonia, $NH_3$ | 0 |
| Solid residue at 180° | 10–50 ,, |
| Total hardness, in French degrees | up to 32 ,, |
| Organic matter (oxygen consumed) | up to 0·25 ,, |

As is seen from this table, to be potable a water should first be quite free from ammonia and nitrites, and should contain only small proportions of nitrates and chlorine and a very small amount of organic matter (expressed as oxygen absorbed). These substances are mainly considered because, although they are quite harmless in the small proportions in which they always occur in water, their presence demonstrates that the water was formerly or is still contaminated by organic matter (sewage water, drainings from inhabited districts, etc.). A water containing ammonia or nitrites or organic matter (beyond the limiting amount) should always be rejected. A water containing nitrates or chlorine beyond the established limits should be suspected, unless it can be proved definitely that these salts come from the soil. The presence of phosphoric acid is also a sign of the organic contamination of water. In special cases as much as 5·0 grams of chlorine per 100 litres may be tolerated, so long as the water exhibits no other defect.

Table II gives the compositions of the water supplies of various towns.

## WATER FOR INDUSTRIAL PURPOSES

Waters for use in industries, for steam boilers, laundries, factories of different kinds, are examined especially with reference to their content of lime and magnesium salts. With such waters it is required to know the content of lime, magnesia, sulphuric acid, and carbonic acid. Further, the quantities of lime and sodium carbonate necessary to correct any excessive hardness of the waters must be known. The addition of lime is necessary to transform the calcium bicarbonate into carbonate, to saturate the free carbonic acid and to precipitate the organic matter; that of soda is required to decompose the calcium sulphate. To eliminate the latter and sulphates in general, barium chloride may also be used.

In practice use has been made and is still made of the results of the hardness determination (*see* Potable Waters: Partial Analysis, 2), but this test gives only approximate and sometimes unexpected results, since it furnishes no information concerning the relation between lime and magnesia, or between carbonates and sulphates. To obtain reliable data it is necessary to carry out—besides various qualitative tests to ascertain if the water is more or less rich in lime, magnesia, carbonates, sulphates, or chlorides—the different determinations indicated for potable waters (*see* Potable Waters, Complete Analysis, 2, 3, 4, 9 and 10), or at least the following tests suggested by Lunge [1] and recognised as of technical value.

**1. Volumetric Estimation of the Total Alkalinity.**—Two hundred c.c. of the water are titrated in the cold with N/5-hydrochloric acid in pres-

[1] Lunge, *Technical Methods of Chemical Analysis* (London, 1908), Vol. I. p. 800.

TABLE II

## Composition of Water Supplies [1]

Parts per 100,000

| Description. | Total Solid Matters. | Organic Carbon. | Organic Nitrogen. | Ammonia. | Nitrogen as Nitrites and Nitrates. | Total Combined Nitrogen. | Chlorine. | Hardness. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Temporary. | Permanent. | Total. |
| *Upland Surface Waters.* | | | | | | | | | | |
| Cardiff Supply, Dec., 1908 . . . . . | 6·28 | 0·160 | 0·016 | 0 | 0·024 | 0·040 | 0·75 | 0·3 | 3·0 | 3·3 |
| Aberdeen Supply, River Dee, March, 1910 . . | 4·76 | 0·193 | 0·026 | 0 | 0·010 | 0·036 | 0·90 | 0·2 | 1·6 | 1·8 |
| Glasgow, Loch Katrine, Nov., 1891 . . . . | 2·80 | 0·149 | 0·025 | 0 | 0·004 | 0·029 | 0·72 | — | — | 0·6 |
| Liverpool, Vyrnwy Water, Average for 1903 . | 4·67 | 0·211 | 0·027 | 0·002 | 0 | 0·029 | 0·87 | — | — | 1·5 |
| Birmingham, Elan Valley Water, Jan., 1911 . | 6·44 | 0·171 | 0·019 | 0 | 0·016 | 0·035 | 0·90 | 0·2 | 2·5 | 2·7 |
| Belfast, Woodburn Supply, Jan., 1910 . . . | 14·40 | 0·325 | 0·022 | Trace | 0·032 | 0·054 | 1·75 | 5·5 | 3·6 | 9·1 |
| *Deep Well and Spring Waters.* | | | | | | | | | | |
| Portsmouth: from Chalk Springs, Aug., 1905 . | 29·80 | 0·032 | 0·009 | Trace | 0·326 | 0·335 | 1·65 | 19·0 | 5·3 | 24·3 |
| Nottingham: New Red Sandstone, Dec., 1910 . | 19·80 | 0·020 | 0·005 | 0 | 0·020 | 0·025 | 1·25 | 9·6 | 7·8 | 17·4 |
| Liverpool: New Red Sandstone, 1903 . . . | 18·43 | 0·024 | 0·007 | 0 | 0·677 | 0·684 | 3·01 | — | — | 7·8 |
| Eastbourne: Chalk, 1911 . . . . . | 28·56 | 0·028 | 0·004 | 0 | 0·378 | 0·382 | 3·63 | 15·1 | 3·8 | 18·9 |
| Great Grimsby: Chalk, 1911 . . . . . | 30·00 | 0·010 | 0·005 | 0 | 0·386 | 0·391 | 1·80 | 18·6 | 3·6 | 22·2 |

[1] From article on "Water" in Thorpe: *Dictionary of Applied Chemistry.*

ence of a few drops of methyl orange solution until a faint red coloration (similar to that given by methyl orange with a saturated solution of carbon dioxide in distilled water) is obtained. The result is expressed in grams of $CaCO_3$ per litre of the water; using 200 c.c. of the water, each 1 c.c. of the N/5-HCl corresponds with 0·05 gram of $CaCO_3$ per litre.

When the water contains sodium carbonate—which is the case, not with ordinary natural waters, but only with certain mineral waters and with waters treated with sodium carbonate—it is necessary to boil a given volume of the water (gradually replacing that which evaporates) until the bicarbonates are decomposed, and then to filter and determine the alkalimetric titre of the filtrate. This alkalinity represents the sodium carbonate existing in the water, together with those minute quantities of the alkaline earth carbonates which remain dissolved (0·036 gram of $CaCO_3$ and 0·1 gram of $MgCO_3$ per litre).[1]

**2. Determination of the Lime and Magnesia.**—Two hundred c.c. of the water are boiled for some minutes with excess of sodium carbonate solution in a porcelain dish and then evaporated to dryness. The residue is heated at 180° and treated with boiling water, the liquid being filtered and the precipitated alkaline earth carbonates washed with a little boiled water and dissolved in excess of N/5-hydrochloric acid. The excess of acid is then titrated with N/5-caustic soda solution in presence of methyl orange. In this case, lime and magnesia are calculated together as CaO; when 200 c.c. of the water are taken, each c.c. of N/5-HCl used corresponds with 0·028 gram of CaO per litre of the water.[2]

**3. Estimation of Sulphates.**—To 200 c.c. of the water, acidified with a little hydrochloric acid, barium chloride is added; if an appreciable precipitate forms after some hours, the sulphuric acid is estimated in the usual way (*see* Potable Waters: Complete Analysis, 4). The sulphuric acid found may be calculated as $CaSO_4$; 1 part of $BaSO_4$ corresponds with 0·5827 part of $CaSO_4$.

**4. Other Tests.**—Where qualitative analysis shows the presence of marked quantities of magnesia, it is well to determine this gravimetrically, the lime being first eliminated by means of ammonium oxalate and the magnesia then precipitated with sodium phosphate and weighed as magnesium pyrophosphate in the ordinary way.

When an appreciable amount of chlorides is indicated qualitatively, the chlorine is determined (*see* Potable Waters: Complete Analysis, 3) and calculated as NaCl.

Also, if qualitative analysis reveals the presence of iron, this may be determined gravimetrically or colorimetrically by Lunge's method (*see* Aluminium Sulphate).

**5. Calculation of the Results.**—The lime (CaO) corresponding with the calcium sulphate found according to 3 is subtracted from the total lime found according to 2; the difference will represent the lime in the

[1] The alkalinity of a water for industrial uses may also be determined by the method indicated for Potable Waters: Partial Analysis, 3.

[2] With waters rich in magnesia it is convenient to follow the method proposed by Wartha and Pfeifer (*Zeitschr. f. angew. chem.*, 1902, p. 193) or that of Gigli (*see* p. 5).

form of carbonate (56 parts of CaO correspond with 100 parts of $CaCO_3$). This furnishes a control of the estimation of the carbonates according to 1, provided always that the magnesia is small in amount; where the magnesia is not negligible, it must be determined separately, as stated under 4.

**6. Removal of the Hardness.**—To obtain an indication of the quantities of lime and sodium carbonate to be added to a water to counteract excessive hardness (*see* p. 12), the following tests may be made:

Clear lime water is prepared and its content of CaO established by means of N/5-HCl in presence of phenolphthalein (1 c.c. N/5-HCl = 0·0056 gram CaO).

To 200 c.c. of the water a few drops of phenolphthalein are added and the standard lime water run in until a red coloration lasting for some instants is formed. From the number of c.c. of lime water used, the amount of lime (CaO) necessary for 1 litre of the water is calculated.

The turbid liquid from the preceding test is filtered and the filtrate treated with a slight excess of N/5-sodium carbonate solution; after a second filtration, the excess of sodium carbonate in the filtrate is titrated with N/5-hydrochloric acid (indicator: methyl orange). From the difference between the number of c.c. of sodium carbonate added and the number of c.c. of hydrochloric acid necessary to neutralise the excess of this carbonate, the amount of sodium carbonate which should be added to the water (as well as lime water) to decompose the calcium sulphate may be calculated, 1 c.c. of N/5-sodium carbonate solution corresponding with 0·0286 gram of $Na_2CO_3 + 10\ H_2O$.

If it is desired to eliminate the sulphates by means of barium chloride, 1 part of $SO_3$ will require 3·25 parts of commercial, crystallised barium chloride (assuming an average of 80% of $BaCl_2$).

***

*Water for steam boilers* should be clear and soft and should not contain too large a proportion of substances which produce incrustations (calcium and magnesium carbonates, gypsum, silica, aluminium, iron) or corrosion (chlorides, nitrates). Boiler water softened by the above methods should be only faintly alkaline (100 c.c. should not require more than 1–1·5 c.c. of decinormal acid for neutralisation) and its hardness should not exceed 3–4 degrees, while with ammonium oxalate it should turn only slightly milky after 1–2 minutes.

*Water for washing silk* should be of low hardness (this is neutralised with a small amount of acetic acid) and should contain no iron and little organic matter.

*Water for washing starch* should be clear, with little organic matter or fixed residue and free from ammonia, nitrites, nitrates and iron.

*Water for sugar factories* should be pure, of low hardness and free from alkali salts—which impede the crystallisation of the sugar—and from organic matter and its decomposition products (nitrites, nitrates and ammonia).

*Water for brewing or distilling* should be clear, odourless, tasteless and neutral; it should have a medium hardness and contain moderate proportions of calcium and magnesium salts and of sulphates; it should contain little chloride or iron and should be as free as possible from organic matter, nitrites, nitrates, ammonia and micro-organisms.

*Water for dyeworks* should exhibit different characters according to the nature of the dyeing; in general it should be very pure and have very little hardness and, especially for delicate colours, should not contain iron.

## CHAPTER II

# CHEMICAL PRODUCTS

The products here treated of are the principal ones of the inorganic and organic chemical industries. Indications are given more particularly of the methods for their evaluation and for the detection of the commoner impurities.

The name of each product is followed by the chemical formula and the atomic or molecular weight referred to O = 16, according to the international atomic weight table for the year 1914.

The products are arranged alphabetically. It must be pointed out that certain other chemical products are dealt with in other chapters (*see* Index at end of Vol. II).

## ACETONE

$C_3H_6O = 58{\cdot}05$

Colourless liquid, of peculiar odour, miscible with water, D = 0·7966 at 15°, b.pt. 55–56°. It may be contaminated with free acids, acetone oil, tarry matters and water, but is usually very pure. The tests to be made are the following:

**1. Density and boiling point**—by the ordinary methods.

**2. Acidity.**—Test with blue litmus paper; any acidity may be determined by titration with decinormal caustic soda in presence of phenolphthalein.

**3. Fixed Residue.**—20 grams are evaporated on a steam-bath; no residue should remain.

**4. Solubility, Moisture.**—Acetone should dissolve in all proportions in water or in light petroleum boiling at 40–60°. Turbidity with water indicates the presence of acetone oil or tarry matter. If drops of water separate at the bottom when the acetone is mixed with light petroleum, water is present.

**5. Tarry Matters.**—5 c.c. of the acetone are treated with a drop of 0·1% potassium permanganate solution; the liquid should remain red for at least 15 minutes if the acetone is pure.

**6. Aldehydes.**—10 c.c. of the acetone are treated with 10 c.c. of distilled water and 2 c.c. of ammoniacal silver nitrate solution (3 grams $AgNO_3$, 3 grams NaOH and 20 grams of ammonia solution of D = 0·9, made up to 100 c.c. with water) and left for 15 minutes in the dark. If there is reduction, the filtered liquid is tested with ammonium sulphide; if a precipitate is formed, the proportion of aldehyde does not exceed 0·1%

**7. Quantitative Determination.**—Messinger's method is used (*see* Methyl Alcohol).

*Commercial* pure acetone should be colourless and neutral, of D not exceeding 0·800 at 15°, should distil to the extent of at least 95% below 58°, and should mix in all proportions with water. It should leave no residue on evaporation, should not decolorise permanganate, and should not contain more than 0·1% of aldehydes.

## ACETONE OILS

These residues from the purification and rectification of crude acetone consist mainly of various higher ketones (methyl ethyl ketone, methyl propyl ketone) and form more or less intensely yellow liquids of peculiar and disgusting odour, acrid, burning taste, D 0·828–0·842, b.pt. very variable according to the quality (75° to 110° or even higher); they are only partly soluble in water but are miscible in all proportions with alcohol. The tests made include distillation, solubility in water, acetone content and bromine absorption.

**1. Distillation.**—A 100 c.c. flask, identical with that used for the distillation of pyridine bases (*see* chapter on Tar and its Products), is used, the distillation being arranged so that the liquid passes over drop by drop; the different fractions corresponding with each 5° C. are collected in graduated cylinders or tubes.

**2. Solubility in Water.**—In a 100 c.c. graduated cylinder are placed 20 c.c. of the oil and 20 c.c. of water. After vigorous shaking, the liquid is allowed to stand until two distinct layers are formed, the number of c.c. of oil dissolved being noted. Sixty c.c. of water are then added and the volume of oil dissolved determined as before. The results obtained are multiplied by 5 and expressed thus:

(*a*) Solubility in an equal volume of water: . . . c.c. per 100 of the oil.

(*b*) Solubility in four volumes of water: . . . c.c. per 100 of the oil.

**3. Ketone Content.**—In this determination, the same liquids are used as in the determination of acetone in crude methyl alcohol, and the same procedure is followed (*see* Methyl Alcohol, Determination of Acetone). Ten c.c. of the oil are made up to 1000 c.c. with water in a graduated flask, which is shaken so as to extract the soluble part of the oil as far as possible. Ten c.c. of the liquid (corresponding with 0·1 c.c. of the oil) are placed in a bottle holding 300–400 c.c. and provided with a ground stopper; 20 c.c. of solution *a* are then added and 50 c.c. of solution *c* run in gradually from a burette. The bottle is tightly stoppered, well shaken and then left for an hour with occasional agitation. Twenty c.c. of solution *b* are next added and the liquid titrated with thiosulphate solution *d* in presence of starch paste.

Thus, by difference, the quantity of iodine, *a*, absorbed by the oil is obtained, the formula,

$$x = \frac{72\ a}{761{\cdot}52} \times 1000,$$

giving the weight of ketones, expressed as methyl ethyl ketone, in 100 c.c.

The percentage by volume is found by dividing this result by the average density of acetone oil, namely, 0·840.

**4. Absorption of Bromine.**—This is carried out as with crude methyl alcohol (*q.v.*).

*
* *

*Acetone oils* vary in composition with the quality of the calcium pyrolignite from which they are obtained, and with the conditions of the distillation, etc.

*Light acetone oils* are yellowish liquids of repulsive odour and burning, acrid taste. They boil in general between 70° and 100° (mostly at 70–80°), are soluble to the extent of 40–50% in an equal volume of water and to the extent of 90–95% in four volumes of water, and contain 90–95% by volume of ketones calculated as methyl ethyl ketone. Light acetone oils are used especially for the denaturation of alcohol and in different countries have to satisfy definite conditions as regards colour, density, boiling point, solubility in water, content of ketones, etc.

*Heavy acetone oils* have a more pronounced yellow colour than the light oils, are less soluble in water, and boil at 130–250°.

## ACETIC ACID

$C_2H_4O_2 = 60{\cdot}03$ (60)

Various qualities are found on the market: *Crude pyroligneous acid*, brown, turbid liquid with a strong empyreumatic odour, D about 1·013, containing 5–10% of acetic acid. *Commercial acetic acid*, colourless or yellowish liquid with more or less marked empyreumatic odour; it may contain 90–95% of acetic acid or may be more dilute (30–60%), the principal impurity being hydrochloric, sulphuric or sulphurous acid. The *pure* or *puriss. glacial acid* is colourless, has a pure acetic odour and contains 96–100% of the acid (D 1·0644–1·0553), the usual content being 96–98% (D 1·0644–1·0604); it boils at about 118° and at about + 10° solidifies to colourless, transparent, lamellar crystals.

Analysis of acetic acids, which may be contaminated with salts of copper, lead, iron and calcium and with arsenic, hydrochloric, sulphuric and sulphurous acids, and organic and pyrogenic substances, comprises mainly the following determinations and tests:

**1. Specific Gravity.**—This is measured in the ordinary manner (hydrometer, Mohr's balance). In the case of a pure acid, the content of acid may be determined from the specific gravity by means of Oudemans' table, which is given in the various books of chemical tables.

**2. Residue on Evaporation.**—10 c.c. are evaporated by gentle heating in a dish to ascertain if any carbonaceous residue (organic matters) remains; this is then calcined, a solid residue showing the presence of mineral substances.

**3. Metals.**—1–2 c.c., diluted with 20 c.c. of water, should not be rendered turbid by hydrogen sulphide (*copper, lead*), or by excess of ammonia and ammonium sulphide (*iron*) or by ammonium oxalate (*calcium*).

**4. Arsenic.**—1–2 c.c., treated with 5 c.c. of *Bettendorf's reagent*,[1] should give no coloration within an hour.

[1] *Bettendorf's reagent* is prepared by dissolving 20 parts of pure tin in 65 parts of pure concentrated hydrochloric acid at a gentle heat, replacing the water evaporated, and saturating with dry, gaseous hydrogen chloride.

**5. Sulphuric and Hydrochloric Acids.**—Separate portions of 1–2 c.c., diluted with 20 c.c. of water, should not be rendered turbid, even after some hours, by barium chloride or by silver nitrate and nitric acid.

**6. Sulphurous Acid.**—After treatment with barium chloride to test for sulphuric acid, the liquid is filtered if necessary and the filtrate oxidised with chlorine or bromine water; the formation of a turbidity indicates the presence of sulphurous acid, which is oxidised to sulphuric acid and thus precipitated by the excess of barium chloride.

**7. Empyreumatic Substances.**—These are readily detected by the smell and taste. Small proportions are tested for by diluting 5 c.c. of the acid with 15 c.c. of water and adding 1 c.c. of 0·1% permanganate solution: the red colour should persist for 10 minutes at least.

**8. Estimation of the Acetic Acid.**—In absence of other acids titration suffices, a few grams of the acid being diluted with water and titrated with normal potash or soda in presence of phenolphthalein; 1 c.c. N-alkali = 0·060 gram of acetic acid. When the acid contains free sulphuric and hydrochloric acids, these must be estimated separately by the ordinary methods.

With acetic acid containing large proportions of empyreumatic substances, Scheurer-Kestner's method [1] is employed: 20 grams of the acid and 50 grams of phosphoric acid (15° Baumé) are distilled slowly from a glass retort. When about one-half of the liquid has distilled over, 25 c.c. of water are added to the retort and the distillation continued until a drop of the distillate fails to redden blue litmus paper. The acetic acid in the distillate is then determined by means of normal soda and phenolphthalein.

## BORIC ACID

$H_3BO_3 = 62{\cdot}02$ (62)

This is sold in white scales (yellowish or brownish if the product is crude) or in a crystalline powder. It dissolves in about 25 parts of cold or 3 of boiling water, and also in alcohol or glycerine.

It may contain sulphates, alkali chlorides, ammonium salts, ferric oxide, alumina, lime, magnesia, silica and organic substances.

**1. Insoluble Substances.**—2–3 grams are dissolved in hot water, the insoluble matter being collected on a tared filter, washed, dried and weighed.

**2. Silica, Chlorides, Sulphates.**—The filtrate from the preceding operation is acidified with nitric acid; one part of the liquid is evaporated to dryness for the detection of *silica*, and others treated with silver nitrate and barium chloride respectively to detect *chlorides* and *sulphates*. With measured volumes of solution, these tests may be made quantitative.

**3. Alumina, Iron, Lime, Magnesia, Alkalies.**—2–3 grams are evaporated to dryness with excess of pure sulphuric and hydrofluoric acids in a platinum dish, the boric acid being thus completely eliminated as boron fluoride. The residue is treated with dilute hydrochloric acid and the solution used for the detection or, if necessary, the estimation of the *iron, alumina, lime, magnesia* and *alkalies*.

[1] *Bull. Soc. chim. de Paris*, 1896, XV, p. 530.

**4. Ammonia.**—This is estimated by distilling with excess of caustic soda (*see* Fertilisers).

**5. Determination of the Boric Acid.**—This is readily effected by Jörgensen's modification of Hönig and Spitz's volumetric method: 10 grams of the acid are dissolved in 500 c.c. of recently boiled water and to 50 c.c. of the solution (1 gram of substance) are added 50 c.c. of pure glycerine (previously neutralised with caustic soda if the reaction is acid) and a few drops of phenolphthalein. The liquid is then titrated with N/2-sodium or barium hydroxide (*absolutely free from carbonates*) until a red coloration is just reached; a further 10 c.c. of the glycerine are added and, if the colour disappears, the titration is continued, this process being repeated until addition of glycerine no longer destroys the red colour. This is the case when 1 mol. of $H_3BO_3$ is combined with 1 mol. of NaOH; 1 c.c. of N/2-alkali = 0·031 gram of $H_3BO_3$.

Commercial *crude* boric acid contains 80–95% $H_3BO_3$ and the *refined* product not less than 99%.

## CARBONIC ACID

$CO_2 = 44$

This is sold in the liquefied condition, compressed in steel cylinders of various capacities. It may contain air, carbonic oxide, mineral acids, empyreumatic substances and various mechanical impurities (especially lubricating oils), which collect at the bottom of the vessel as a thick, brown liquid of repulsive odour. Analysis comprises the following:

**1. Gaseous Impurities.**—The gas is introduced into a graduated cylinder over mercury [1] and there left in contact with a few c.c. of boiled, concentrated caustic soda solution; the residual unabsorbed gas represents the gaseous impurities of the carbonic acid. According to Werder,[2] the carbonic acid may be passed through an Orsat apparatus with three absorption bulbs, the first containing potassium hydroxide solution to absorb the carbon dioxide, the second potassium pyrogallate solution to absorb the oxygen and the third ammoniacal cuprous chloride solution for the carbon monoxide.

**2. Empyreumatic Substances.**—A current of the gas is passed through concentrated sulphuric acid; if the gas is impure, the acid becomes brown.

**3. Sulphurous and Nitrous Acids.**—If either of these is present, passage of the gas through potassium permanganate solution gradually decolorises the latter.

**4. Hydrochloric Acid.**—When this is present, passage of the gas through a dilute silver nitrate solution acidified with nitric acid renders the liquid turbid.

As a rule the acid of commerce is moderately pure and contains only small proportions of air (up to 6%), and rarely carbon monoxide (up to 4%). A good carbonic acid should contain at least 98% by volume of $CO_2$ and not more than 0·5% of CO, and should be free from mineral acids and empyreumatic substances.

[1] Instead of a cylinder over mercury, a Winkler burette or any other form of gas-measuring apparatus may be used.

[2] *Chem. Zeit.*, 1906, p. 1021.

## CHROMIC ACID

$CrO_3 = 100$

Pure chromic acid forms dark ruby-red, silky, acicular crystals, but that used technically is in much smaller crystals or in red crystalline masses. The impurities present are mainly sulphuric acid and alkali salts, more rarely nitric acid and barium and lead salts.

**1. Sulphuric Acid.**—1 gram in 20 c.c. of water should give a clear solution, which is not rendered turbid by addition of hydrochloric acid and barium chloride.

**2. Alkali Salts.**—0·1 gram is heated to redness and the residue treated with water and filtered; if the filtrate is yellow, alkali salts are present.

**3. Nitric Acid.**—1 gram is dissolved in water and the liquid treated with sulphurous acid solution until it becomes distinctly green and then with ammonia; the liquid is boiled and filtered, and the filtrate (which should be colourless) tested for nitric acid in the usual way.

**4. Barium or Lead Salts.**—A few grams are treated with water and a few drops of dilute sulphuric acid; after standing, the clear liquid is decanted and any residue examined for lead or barium sulphate.

**5. Determination of the Chromic Acid.**—About 0·1 gram is boiled with hydrochloric acid and the liberated chlorine collected in potassium iodide solution. The iodine set free by the chlorine is then estimated by means of sodium thiosulphate solution and starch paste (1 c.c. of N-thiosulphate = 0·03339 gram $CrO_3$).

Even " pure " chromic acid generally contains small proportions of sulphuric acid or sulphates. In the commercial product as much as 30% of potassium sulphate has been found (Krauch).

## CITRIC ACID

$C_6H_8O_7 + H_2O = 210$

Large, colourless, odourless, non-hygroscopic crystals of acid taste, soluble in water and alcohol and, to a less extent, in ether. They may contain tartaric, oxalic and sulphuric acids and salts of calcium, iron and heavy metals (especially lead and copper).

**1. Tartaric Acid.**—1 gram of the acid is dissolved in 2 c.c. of water and the solution treated with potassium acetate and alcohol: no turbidity should be produced. Very small amounts may be detected by dissolving 1 gram of the acid in 10 c.c. of distilled water and gradually pouring part of the solution into 15–20 c.c. of lime water, which should remain clear.

**2. Oxalic Acid.**—1 gram of the acid, dissolved in 10 c.c. of water, should not be rendered turbid by addition of calcium sulphate solution.

**3. Sulphuric Acid and Sulphates.**—The aqueous solution (1 : 10) should not be rendered turbid by addition of barium chloride and hydrochloric acid.

**4. Lime.**—The aqueous solution (1 : 10), neutralised with ammonia, should not be rendered turbid by addition of ammonium oxalate.

**5. Ash.**—10 grams of the acid are carefully burned in a crucible and

the ash weighed. If this exceeds 0·5%, a greater quantity of the acid is burned and the ash tested for lead, copper and iron.

**6. Lead.**—Of particular importance is the determination of the lead, the presence of which in small quantities is due to the crystallisation vessel. Warington's colorimetric method is used:

A standard lead solution is prepared by dissolving about 50 grams of ammonium citrate (puriss.) and 0·016 gram of lead nitrate (corresponding with 0·01 gram Pb) in water and making up to 500 c.c. From this a scale of tints is prepared by diluting varying volumes of the liquid (e.g., 1, 2, 3, 5, 10, 15, 20 c.c., etc.) to 50 c.c. and adding to each a drop of ammonium sulphide.

Forty grams of the citric acid are dissolved in water and slight excess of ammonia added, the cooled liquid being diluted to 500 c.c. To 50 c.c. of this solution is added a drop of ammonium sulphide, the coloured liquid thus obtained being compared with the above colour scale. The judging of the colours is aided by addition of a little glycerine, which renders the colours sharper and prevents the formation of precipitate. In this way the lead content of citric acid may be determined with great accuracy.

**7. Determination of the Citric Acid.**—In absence of other acids, it suffices to dissolve 1–2 grams of the acid in water and to titrate the solution with normal potassium hydroxide solution in presence of phenolphthalein; 1 c.c. of N-alkali = 0·07 gram of crystallised citric acid ($C_6H_8O_7 + H_2O$) and 14·5 c.c. of N-alkali = 1 gram of the crystallised acid.

In presence of other acids, usually oxalic and tartaric, these extraneous acids must be separated and, if necessary, estimated:

(*a*) PRESENCE OF OXALIC ACID.—2–3 grams of the citric acid, are dissolved in water and neutralised with caustic soda; the liquid is acidified with acetic acid and a solution of calcium sulphate or chloride added. The calcium oxalate formed is filtered off, washed with hot water and weighed as carbonate or oxide. In the filtrate the citric acid is determined by precipitation as indicated under analysis of lemon juice (*see* later, 4). Where determination of the oxalic acid is unnecessary, this precipitation method is applied directly to 2 grams of the acid.

(*b*) PRESENCE OF TARTARIC ACID (Allen's method).—2 grams of the citric acid are dissolved in 20 c.c. of 57% alcohol, the liquid being filtered if necessary and made up to 45 c.c. with alcohol of the same strength; 5 c.c. of a cold, saturated solution of potassium acetate in 57% alcohol are then added and the liquid shaken for 10 minutes. The presence of tartaric acid leads to the formation of insoluble acid potassium tartrate, which may be collected on a filter, washed first with cold saturated potassium bitartrate solution and then with 57% alcohol, dried at 100° and weighed. The weight, multiplied by 0·8, or the number of c.c. of normal alkali used for its titration, multiplied by 0·150, gives the amount of tartaric acid contained in the 2 grams of substance taken. In the filtrate from the bitartrate the citric acid is determined as in lemon juice.

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**Citric acid should dissolve completely in water or alcohol without leaving**

any trace of calcium sulphate. Its crystals should not be deliquescent owing to the presence of traces of sulphuric acid. It may give 0·05–0·25% of ash; it is always necessary to test for copper and lead, and to determine the latter. The presence of these poisonous metals is accidental, and as a rule they do not exceed 0·01% in commercial citric acid. The proportion of lead varies somewhat; samples of English origin have shown from 0·0018 to 0·024%, French and German samples from 0·0006 to 0·0029%, and American samples from 0·003 to 0·0063%. According to some authorities the maximum limit allowable should be 0·002% of lead, whilst others give 0·5 m. grm. per 100 grams. Not infrequently commercial citric acid is adulterated with tartaric acid.

## Lemon Juice, etc.

The juice pressed from lemons contains citric acid and is used mainly for the preparation of calcium citrate and thus of citric acid. The crude juice (*agro crudo*) is a greenish-yellow liquid with an acid taste resembling that of the lemon in the fresh juice; later the taste becomes bitter. The concentrated juice (*agro cotto*) is a dense, syrupy, brown liquid with an odour recalling that of caramel and a bitter, highly acid flavour.

The bergamot and wild lemon (*Citrus limetta*) also give crude and concentrated juice, which differ somewhat in objective properties from that of the lemon; bergamot juice, prepared specially in Calabria, is also used for making calcium citrate.

Analysis of the juice includes determinations of the specific gravity, free acidity, citric acid and other organic acids united with bases, true citric acid, alcohol and adulterants, these being usually free mineral acids or salt water.

**1. Specific Gravity.**—This is measured with a hydrometer or a Mohr's balance. Use is also made of a *citrometer*, which is a hydrometer on which 60 degrees corresponds with the specific gravity 1·24, this being a standard for concentrated juice.

**2. Free Acid.**—50 c.c. of the concentrated juice are diluted to 500 c.c. with water and 25 c.c. (= 2·5 c.c. of juice), then titrated with N/2-soda, using neutral litmus paper as indicator. With the non-concentrated juice, 10 or 20 c.c. are taken directly. In any case, before complete neutralisation, when about five-sixths of the free acidity has been neutralised, the liquid is boiled for a few minutes and the titration then concluded. The acidity is calculated as crystallised citric acid; 1 c.c. N/2-alkali = 0·035 gram of $C_6H_8O_7 + H_2O$. To give the result in ounces per gallon, after the English way, the percentage found is multiplied by 1·60.

**3. Citric and other Organic Acids combined with Bases.**—The neutral solution remaining from the preceding determination is evaporated to dryness and the residue, after cautious incineration, treated with water and with a measured volume of N-sulphuric acid; after boiling and filtering, the excess of sulphuric acid in the filtrate is determined by titration with N-alkali. The amount of sulphuric acid used to neutralise the ash is equivalent to the total organic acids in the substance, since all the organic salts are transformed into carbonates on incineration. Hence, if the total acids are calculated as citric acid (1 c.c. of N-sulphuric acid = 0·070 gram of crystalline citric acid, $C_6H_8O_7 + H_2O$) and from this is deducted the free

citric acid found in the preceding determination, the result is the combined citric acid (and other acids).

**4. True Citric Acid.**—From 15 to 20 c.c. of non-concentrated or about 3 c.c. of concentrated juice are weighed out and neutralised exactly with approximately 2N-caustic soda solution. The liquid is diluted to about 50 c.c. and 20 c.c. of about 40% pure calcium chloride solution added; the whole is then acidified with a few drops (4–6) of seminormal hydrochloric acid, the subsequent procedure being exactly as described for the determination of citric acid in calcium citrate (*see* Calcium Citrate, 6, second paragraph).

**5. Alcohol.**—Any alcohol present in the juice is determined by distillation in the usual way (*see* Wines, Vol. II).

**6. Sulphuric, Hydrochloric and Nitric Acids.**—These acids and their salts are tested for by the ordinary reagents or by the tests given for free mineral acids in vinegar (*see* Vinegar, Vol. II). According to Scribani,[1] nitric acid is easily detected by adding to the juice (diluted if too highly coloured) a little hydrochloric acid solution of ferrous chloride free from ferric salt, boiling and then adding potassium thiocyanate solution; if nitric acid is present in the juice, a red coloration is formed owing to oxidation of the ferrous salt.

**7. Sulphurous Acids, Sulphites.**—The clear, more or less yellow juices intended for the preparation of syrups and beverages may contain sulphurous anhydride added as preservative.

(*a*) *Qualitative Test.* 50–100 c.c. of the juice are introduced into a flask which is closed by a cork slit at the bottom to allow of the insertion of a freshly prepared starch-iodide paper[2] moistened at the extremity; if the flask is heated gently, the paper will assume a blue or brown colour if sulphurous acid or a sulphite is present.

(*b*) *Quantitative Determination.*—From 50 to 100 c.c. of the juice mixed with 5 c.c. of 20% phosphoric acid are distilled in a current of carbon dioxide. From 25 to 50 c.c. of distillate are collected in 50 c.c. of N/10-iodine solution contained in a flask with a doubly-bored stopper, through which pass the condensing tube and a second tube leading to a U-tube charged with a definite volume of N/50-sodium thiosulphate solution (say, 10 c.c.). At the end of the distillation, the contents of this tube are washed into the iodine solution and the excess of iodine titrated with the sodium thiosulphate.

The number of c.c. of iodine solution used up in oxidising the sulphurous acid, multiplied by 0·00064, gives the quantity of sulphur dioxide in the juice.

The sulphur dioxide may also be determined gravimetrically on the distilled product collected in the iodine solution (*see* Beer, Vol. II).

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Besides free citric acid, which represents 88–98% of the total acidity, *lemon juice*, etc., contains small proportions of citrates, other free organic acids and

[1] *Gazzetta chimica italiana*, 1878, VIII, p. 234.

[2] The solution for the preparation of this paper is made from 0·1 gram of potassium iodide and 1 gram of starch in 100 c.c. of distilled water.

their salts, iron, mineral salts, saccharine substances, albuminoids, gummy matters, etc., and sometimes alcohol (up to 1·5% by volume). *Concentrated lemon juice* contains about 40% of citric acid and has the density 1·2–1·4. The crude juice has the density 1·03–1·04 and contains variable proportions of citric acid (4–7%). The crude and concentrated juices from the bergamot contain less citric acid than lemon juice (about 30% in the concentrated juice).

These juices may be adulterated with salt, which increases the density, or with sulphuric, tartaric or nitric acid, which increases the acidity. The pure juices should contain only traces of sulphates and chlorides.

These juices are usually quoted in English measures, the unit of volume being taken as the pipe of 108 imperial gallons (1 gallon = 4·536 litres) and that of weight as the ounce (28·35 grams). The crude juice is quoted on the basis of 11 ozs. of citric acid per gallon, and the concentrated juice on the basis of 66·87 ozs. of free crystallised citric acid ($C_6H_8O_7$, $H_2O$) or 64 ozs. of the acid, $C_6H_8O_7$, $\frac{1}{2}$ $H_2O$. Bergamot juice is generally quoted on the basis of 48 ozs. per gallon.

## FORMIC ACID

$H_2CO_2 = 46$

In the pure state this is a colourless liquid of particularly pungent odour, D = 1·225–1·227 (at 15°), b.pt. 100°; it is extremely soluble in water and at 0° solidifies to crystals which melt again at about 8°. It is placed on the market in various concentrations, up to almost 100%, but usually 85% (D = 1·202).

It may contain mineral acids (especially hydrochloric acid), acetic acid (mixtures of formic acid with varying proportions of acetic acid are sold as *acetargol*), oxalic acid, salts of the alkalies and heavy metals (lead, copper, iron), arsenic (occasional traces), acrolein, allyl alcohol and empyreumatic substances. The following tests are made.

**1. Mineral Acids.**—10 c.c. of the acid are diluted with 100 c.c. of water, 50 c.c. being then treated with silver nitrate (in the cold) and 50 c.c. with barium chloride.

**2. Acetic Acid.**—1–2 c.c. of the acid, diluted with 20 c.c. of water and mixed with 6 grams of yellow mercuric oxide, are heated on the water-bath until evolution of gas ($CO_2$) ceases and the liquid then filtered. In the case of pure formic acid, the filtrate has a neutral reaction (all the formic acid being decomposed), but in presence of acetic acid the filtrate is acid and permits of the identification of the acetic acid by the odour.

The *quantitative* determination of acetic acid when mixed with formic acid may be effected by Hamel's method: 3–4 grams of the acid are neutralised with N-sodium hydroxide (towards phenolphthalein), the liquid evaporated to dryness on a water-bath and the residue dried in an oven at 120–130° and weighed. It is then treated with excess of pure formic acid (which liberates acetic acid from its salts), again evaporated to dryness, the residue being then taken up in a little water, once more evaporated and the residue dried at 120–130° and weighed. From the difference between the two weights the acetic acid is calculated.

**3. Oxalic Acid.**—2 c.c. of the acid are diluted with 20 c.c. of water and the liquid rendered alkaline with ammonia and treated with calcium chloride; a turbidity indicates oxalic acid.

**4. Various Mineral Salts.**—10 c.c. of the acid, evaporated on a steam-

bath, should leave no appreciable residue, and 2 c.c., diluted with 20 c.c. of water and rendered alkaline with ammonia, should undergo no change with ammonium sulphide.

**5. Acrolein, Allyl Alcohol, Empyreumatic Products.**—These are recognised by the odour, after neutralisation of the acid with sodium hydroxide.

**6. Determination of the Formic Acid.**—This may be effected by titration with normal alkali solution in presence of phenolphthalein (1 c.c. N-alkali = 0·046 gram of $H_2CO_2$) and controlled by the specific gravity of the sample. A marked difference between the two results indicates extraneous acids or salts.

The formic acid may be determined directly as follows: 1–2 grams of the acid are neutralised exactly with sodium hydroxide, treated with an excess of mercuric chloride solution and heated on a steam-bath. The mercurous chloride thus formed is then collected on a tared filter, washed, dried and weighed (1 gram $Hg_2Cl_2$ = 0·0977 gram of $H_2CO_2$).

For determining the formic acid in *formates*, the latter are decomposed by phosphoric acid and distilled, the formic acid in the distillate being determined as above.

Almost pure formic acid, containing only traces of hydrochloric acid and sodium sulphate, may now be purchased. Some of the less pure forms contain up to 2% of hydrochloric acid. The mixtures with acetic acid (acetargol) have been already mentioned.

## HYDROCHLORIC ACID

$HCl = 36·46$ (36·5)

The *crude acid* of commerce is more or less yellow, D about 1·18, containing about 35% HCl. The *pure acid* is colourless and the most concentrated has D=1·19—1·20 with a content of 37–39% HCl.

The crude acid may contain sulphuric acid, chlorine, bromine, iodine, arsenic, iron, lime, alkalies, and organic matter. The pure acid may contain the same impurities but naturally in smaller proportions.

Its analysis includes the following:

**1. Fixed Residue.**—50 c.c. are evaporated in a platinum dish and the residue, if appreciable, weighed.

**2. Sulphuric and Sulphurous Acids.**—10 c.c., diluted with 50 c.c. of water, are treated with barium chloride; no turbidity should appear even after 12 hours. Addition of a few drops of chlorine water to the liquid, filtered if necessary, will cause turbidity if sulphurous acid is present.

Sulphurous acid may also be detected by treating the acid with a piece of pure zinc and testing the gas evolved for hydrogen sulphide by means of lead acetate paper.

The sulphuric acid may be determined quantitatively by precipitation as barium sulphate (1 gram $BaSO_4$ = 0·34335 gram $SO_3$).

**3. Arsenic.**—1 c.c. of the acid is treated with 5 c.c. of Bettendorf's reagent (*see* note on p. 18) and note made if the liquid colours within an hour.

For the quantitative determination of arsenic in the crude acid, 20 c.c. are diluted with as much water and approximately neutralised with sodium carbonate. A little ammonia and then yellow ammonium sulphide are added and after acidifying with pure hydrochloric acid, the liquid is heated on a steam-bath and a current of hydrogen sulphide passed through it for 2 hours. The precipitated arsenic sulphide is collected, washed, dissolved in potassium hydroxide solution, oxidised with bromine, precipitated with magnesia mixture and weighed as magnesium pyroarsenate. 1 gram of the pyroarsenate = 0·48387 gram As.

**4. Metals.**—10 c.c., diluted with 50 c.c. of water, are treated with hydrogen sulphide, with ammonia and ammonium sulphide, and with ammonium oxalate ; pure acid exhibits no change with these reagents. *Iron* is also easily detected by means of potassium ferrocyanide (deep blue coloration or precipitate).

**5. Chlorine.**—5 c.c. of dilute, fresh starch paste are treated with a few drops of 10% potassium iodide solution absolutely free from iodate and a few drops of dilute sulphuric acid. On addition of 1 c.c. of the hydrochloric acid, diluted with water, a blue coloration forms in presence of free chlorine.

**6. Bromine and Iodine or the Corresponding Acids.**—20 c.c. of the acid are neutralised with soda and evaporated to dryness, the residue being taken up in a little water, a little fresh chlorine water added and the liquid shaken with carbon disulphide ; in presence of bromine or iodine the carbon disulphide becomes yellow or violet.

**7. Determination of the Hydrochloric Acid.**—With the pure acid, it is sufficient to determine the acidity with a standard alkali (1 c.c. N-alkali = 0·0365 gram HCl) or to measure the specific gravity and then deduce the acid content by means of tables. When the acid is not pure, the estimation is made by precipitating with silver nitrate either gravimetrically or volumetrically by Volhard's method (*see* p. 10).

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The crude acid may contain marked amounts of sulphuric acid (up to about 3% $SO_3$), but for technical purposes the content should not exceed 1·5%. Considerable quantities of arsenic (up to 10 grams per 100 kilos, according to Buchner) may also be found and small amounts of iron. The pure acid may contain traces of sulphuric acid which should not, however, exceed 1 m. grm. per 100 grams of the acid ; no trace of arsenic, iron or chlorine should be present. According to the Italian Pharmacopœia, 10 c.c. should leave no trace of residue on evaporation.

## HYDROFLUORIC ACID

HF = 20

Aqueous solutions containing 60–65% by weight of HF (D = 1·23–1·263) or 50% or 40% (D = 1·189 – 1·151) are sold. It is a colourless liquid, fuming in the air, of irritating caustic odour. It is kept in vessels of gutta-percha, hardened rubber or, better, of paraffin. It may be contaminated with sulphuric, hydrochloric, nitric and hydrofluosilicic acids, arsenic, heavy and earthy metals and organic matter (derived especially from the vessels).

**1. Sulphuric Acid.**—3 grams, diluted with 10 c.c. of water, are treated with 2 c.c. of conc. hydrochloric acid and a few drops of barium chloride solution: no turbidity should be produced within an hour.

**2. Hydrochloric Acid.**—2 grams, diluted as above, are treated with silver nitrate: no opalescence should result.

**3. Nitric Acid.**—To 4–5 c.c. of the acid are added a little copper turnings and about 1 c.c. of conc. sulphuric acid; the liquid is then heated and any evolution of red fumes observed.

**4. Hydrofluosilicic Acid.**—To 4–5 c.c. of the acid is added saturated potassium chloride solution: in presence of hydrofluosilicic acid, a white, gelatinous precipitate is formed.

**5. Arsenic, Heavy Metals, etc.**—5 grams of the acid are diluted with 20 c.c. of water, the liquid heated and a current of hydrogen sulphide passed through: a yellow (arsenic) or brown precipitate (heavy metal) may be formed.

5 grams are diluted with 50 c.c. of water, rendered alkaline with ammonia and treated separately with ammonium sulphide, ammonium carbonate and ammonium phosphate for the detection of iron, lime and magnesia.

**6. Fixed Residue.**—10 grams are evaporated in a platinum dish.

**7. Organic Matter.**—Acid containing this decolorises potassium permanganate solution.

The pure acid should leave no weighable fixed residue.

## HYDROFLUOSILICIC ACID

$H_2SiF_6 = 144{\cdot}3$

This occurs commercially in 7–10% solution (D = 1·05–1·08) or in greater concentrations up to 20 or about 35% (D = 1·17–1·33). It may contain sulphuric acid and heavy metals as impurities.

**1. Sulphuric Acid.**—5 c.c., diluted with an equal volume of water, and treated with strontium nitrate solution (free from barium), should not become turbid, even on standing.

**2. Metals.**—5 c.c. should leave no appreciable residue on evaporation in a platinum dish. 5 c.c., diluted with as much water and a few drops of hydrochloric acid, should remain unchanged by hydrogen sulphide, even after being rendered alkaline with ammonia.

**3. Quantitative Determination.**—This is effected by precipitating as potassium fluosilicate or by titration with N/2-alkali at the boiling point in presence of phenolphthalein, or in the cold in presence of methyl orange and 25 c.c. of 22% calcium chloride solution. 1 c.c. N/2-alkali = 0·012 gram $H_2SiF_6$.

## LACTIC ACID

$H_6C_3O_3 = 90$

A syrupy, odourless, colourless, highly acid liquid, soluble in all proportions in water, alcohol or ether, but insoluble in benzene or chloroform. The pure acid generally contains 75–80% of the acid (D = 1·21–1·23), the

remainder being water. The crude acid, also found on the market, is yellowish or brown and contains 20–50% of the acid. The ordinary impurities are various mineral acids and salts, organic acids (acetic, butyric, tartaric, citric), sugars, glycerine, mannitol.

**1. Extraneous Acids.**—The acid diluted in the proportion 1 : 10 and acidified with nitric acid, should give no turbidity with barium nitrate (*sulphuric acid* or *sulphate*) or with silver nitrate (*hydrochloric acid* or *chloride*).

1 part of the acid is diluted with 5 parts of 96% alcohol and filtered, the filtrate being treated with a little hydrochloric acid and a few c.c. of 10% calcium chloride solution and boiled: the presence of *free sulphuric acid* is indicated by a turbidity appearing either immediately or after a short time.

When distilled with steam, the acid should give a distillate which is not rendered turbid by silver nitrate (*free hydrochloric acid*).

1 c.c. of the acid, neutralised with about 60 c.c. of lime water, should not become turbid either in the cold (*oxalic, tartaric* or *phosphoric acid*) or in the hot (*citric acid*).

1 c.c., gently heated, should not evolve an odour of fatty acids (*acetic, butyric acids*).

**2. Mineral Salts.**—The acid diluted in the proportion 1 : 10 should not change with hydrogen sulphide, or ammonia and ammonium sulphide or oxalate, or potassium ferrocyanide (*copper, lead, zinc, calcium, iron*).

10 c.c., carefully calcined, should leave no appreciable residue.

**3. Various Impurities.**—1 c.c., poured by drops into 2 c.c. of ether, should dissolve to a clear liquid (absence of *sugars, mannitol, gum, calcium phosphate*, etc.).

1 c.c., neutralised with magnesium oxide, evaporated to dryness on a steam bath, and the residue taken up in absolute alcohol, filtered and evaporated, should leave no sweet, syrupy residue (*glycerine*).

1 c.c., mixed carefully (avoiding rise of temperature) with 1 c.c. of conc. sulphuric acid, should not produce a brown coloration (*sugars*).

**4. Quantitative Determination.**—In absence of other acids, the lactic acid may be estimated by means of a standard alkali: to 10 c.c. (or 10 grams) are added 20 c.c. of N-sodium hydroxide and a few drops of phenolphthalein and the liquid boiled for 10 minutes and the excess of alkali titrated with normal hydrochloric acid: 1 c.c. N-NaOH = 0·09 gram $C_3H_6O_3$.

With crude, impure products, the lactic acid is estimated by Ulzer and Seidel's method,[1] which consists in oxidising by means of alkaline potassium permanganate and then determining the oxalic acid formed. The presence of oxalic acid or of glycerine must, of course, be excluded.

## NITRIC ACID

$HNO_3 = 63$

This is found in commerce as *crude* or *commercial acid*, usually yellowish, D = 1·33–1·40, containing 52–65% $HNO_3$; as *pure acid*, which is colourless

[1] *Chem. Zeit.*, 1897, p. 204.

and of variable specific gravity but usually 1·4 or 1·5–1·52, containing 65% or 94–99·5% $HNO_3$; as *fuming acid*, which is reddish-yellow or reddish-brown and emits dense reddish fumes in the air, D = 1·48–1·52 (86–99% $HNO_3$) and is a mixture of nitric acid with nitrogen tetroxide and nitrous acid (the latter in small quantity, especially in the very dark fuming acid).

The usual impurities to be sought for in nitric acid are: sulphuric and hydrochloric acids, heavy, earthy and alkali metals, iodine and its compounds and nitrous compounds.

**1. Sulphuric Acid.**—10 c.c. are evaporated on a steam-bath to 1 c.c., then diluted with 10 c.c. of water and tested with barium nitrate: no turbidity should appear.

**2. Hydrochloric Acid.**—1 c.c., diluted with 5 c.c. of water, should give no turbidity with silver nitrate.

**3. Metals.**—Diluted in the ratio 1 : 2 and rendered alkaline with ammonia, the acid should not be changed by ammonium sulphide or oxalate.

1 c.c., diluted with 10 c.c. of water, should give no immediate coloration with potassium ferrocyanide (*iron*).

50 c.c., evaporated on a steam-bath, should give no appreciable residue.

**4. Iodine (Iodic Acid).**—1 c.c., diluted with 2 c.c. of water and shaken with a few drops of chloroform, should give no coloration to the latter, even after addition of a fragment of zinc.

**5. Nitrous Compounds.**—To 5 c.c. of the acid, diluted with 5 volumes of water, are added a few drops of normal potassium permanganate solution, which is decolorised if nitrous compounds are present.

For the quantitative determination of nitrous compounds in the fuming acid, Lunge and Marchlewski's method may be followed: From a well-calibrated, narrow burette, divided into $\frac{1}{20}$ c.c. so that 0·01 c.c. can be readily measured, the acid is allowed to fall drop by drop into a measured volume of seminormal permanganate solution (15·803 grams $KMnO_4$ per litre) kept at 40°, until decolorisation occurs. Before the titration the acid is left for some time in the burette to assume the air-temperature, which is measured with an accurate thermometer. The number of c.c. of acid taken, multiplied by its specific gravity determined at the temperature of titration, gives the weight of acid used in the titration. The nitrous compounds, calculated as $N_2O_4$, are expressed per 100 parts of the acid. The titre of the permanganate is determined by means of iron in the ordinary way. 1 c.c. N/2-permanganate = 0·023 gram $N_2O_4$.

In acid for technical purposes the presence of nitrous products is allowed —in that used in dynamite factories to the extent of 2% (Guttmann).

## OXALIC ACID

$$H_2C_2O_4 + 2H_2O = 126{\cdot}05 \quad (126)$$

Colourless crystals, soluble in about 10 parts of cold water or 2·5 of boiling water, and in alcohol. Its most frequent impurities are sulphates, chlorides, ammonia, alkalies and calcium, and sometimes small quantities of copper, lead and iron.

**1. Sulphates, Chlorides.**—Separate portions of the 1 : 10 solution, acidified with nitric acid, should not become turbid with barium chloride or silver nitrate.

**2. Ammonia.**—2 grams, heated with excess of caustic soda, should yield no ammoniacal odour.

2 grams dissolved in 30 c.c. of water, neutralised with sodium hydroxide and made up to 50 c.c., should give no coloration with 10–15 drops of Nessler solution.

**3. Metals.**—The 1 : 10 solution should not become turbid (*calcium*) when rendered alkaline with ammonia or after further addition of ammonium sulphide (*copper, lead, iron*).

10 grams, heated in a platinum crucible, should volatilise without turning brown or leaving appreciable residue. Any residue left should be tested for alkali metals.

## PHOSPHORIC ACID

$H_3PO_4 = 98{\cdot}024$ (98)

*Ordinary phosphoric acid* or *orthophosphoric acid* is a colourless, odourless liquid with density varying according to the concentration (1·73 = 90%; 1·72 = 86%; 1·44 = 60%; 1·35 = 50%; 1·26 = 40%; 1·15 = 25%). The impurities to be tested for in the commercial acid are: sulphuric, nitric, hydrochloric, metaphosphoric and phosphorous acids, ammonia, arsenic, heavy and earthy metals and organic matter.

**1. Sulphuric Acid.**—The dilute acid (1 : 2) is treated with barium chloride in the hot: no turbidity should appear, even after standing.

**2. Nitric Acid.**—The dilute acid (1 . 1) is treated with a few drops of a sulphuric acid solution of diphenylamine: no blue coloration should appear. 1 c.c. of the acid + 3 c.c. of water should not decolorise a drop of a sulphuric acid solution of indigo.

**3. Hydrochloric Acid.**—The acid, diluted with 5 vols. of water and treated with silver nitrate in the cold, should give no turbidity.

**4. Phosphorous Acid.**—To the acid, somewhat diluted, silver nitrate is added and the liquid heated to boiling; in presence of phosphorous acid, blackening is observed. Also, the acid is heated with mercuric chloride, which gives a white precipitate of calomel in presence of phosphorous acid.

**5. Metaphosphoric Acid.**—The diluted acid is added to a dilute solution of albumin: a turbidity is formed if metaphosphoric acid is present.

**6. Ammonia.**—The acid is heated with excess of caustic soda and the odour of the evolved vapour noted.

**7. Arsenic.**—When tested for an hour in the Marsh apparatus (*see* Flesh Foods, Vol. II), the acid should give no arsenic ring; 1 c.c. of the acid with 5 c.c. of Bettendorf's reagent (*see* note on p. 18) should give no coloration within an hour.

**8. Heavy and Earthy Metals.**—The acid is subjected to a current of hydrogen sulphide. Another portion, greatly diluted, is rendered alkaline with ammonia and then tested with ammonium sulphide, ammonium

oxalate, etc. A third portion is mixed with 4 vols. of alcohol. In no case should a precipitate form.

**9. Organic Matter.**—When strongly heated in a dish, the acid blackens if organic substances are present. 5 c.c. of the acid are boiled for 5 minutes with 5 c.c. of dilute sulphuric acid and 5 drops of 0·1% permanganate: in presence of organic matter, the liquid becomes decolorised (the decoloration may, however, depend on lower acids of phosphorus, arsenious acid, etc.).

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*Metaphosphoric* or *glacial phosphoric acid* ($HPO_3 = 80$) is sold in glassy masses or rods. It may contain the same impurities as ordinary phosphoric acid but is contaminated more particularly with sodium metaphosphate, often in considerable quantities. This impurity is detected by dissolving the acid in concentrated hydrochloric acid (D = 1·19): the presence of the sodium salt leads to the formation of sodium chloride, which remains undissolved.

## PICRIC ACID

$H_3C_6N_3O_7 = 229$

Lemon-yellow, crystalline scales or powder, m.pt. 122–123°, soluble in 25 parts of cold water, readily soluble in boiling water, alcohol, ether or benzene. The commercial acid may contain, as impurities, resinous matters, oxalic acid, sulphates, chlorides and mono- and di-nitrophenols, and may be adulterated with considerable quantities of alum, magnesium sulphate, sodium sulphate and sodium chloride.

**1. Resinous and Various Insoluble Substances.**—4 grams of the acid are boiled with 100 c.c. of water until completely dissolved, any insoluble residue being collected on a tared filter and weighed.

**2. Various Mineral Salts.**—4 grams of the acid are treated with 100 c.c. of ether, any insoluble residue being collected, weighed and analysed, tests being made especially for magnesium sulphate, alum, sodium sulphate and sodium chloride.

**3. Oxalic Acid.**—4 grams dissolved in hot water (about 250 c.c.) are neutralised with ammonia and tested with calcium chloride.

**4. Sulphuric Acid.**—4 grams, dissolved in 250 c.c. of water, are tested with barium chloride.

**5. Hydrochloric Acid.**—4 grams, dissolved in 250 c.c. of water and acidified with nitric acid, are tested with silver nitrate solution.

**6. Mono- and di-nitrophenols.**—Into two bottles with ground stoppers are poured equal volumes of 1% bromine water, into one of them a 1% solution of the picric acid and then into each excess of potassium iodide. The iodine liberated in each case is titrated with N/10-thiosulphate and from the bromine combined the content of these two impurities calculated.

The pure acid should not leave more than 0·1% of residue insoluble in water or 0·2% insoluble in ether. Only traces of oxalic acid or hydrochloric acid should be found, and the sulphuric acid should not exceed 0·05%.

## SULPHURIC ACID

$H_2SO_4 = 98{\cdot}08$ (98)

This is sold in various degrees of concentration and purity: *Chamber acid* of 50–53° Baumé, D = 1·53–1·58, with 62–67% $H_2SO_4$; acid of 60° Baumé, D = 1·71, with 78% $H_2SO_4$; ordinary English acid of 66° Baumé, D = 1·84, with 93–96%; extra concentrated, with 96–98% and the monohydrate, with 99·5%. As regards the purity, there is more or less impure commercial acid, containing more especially lead, iron, arsenic, sulphurous acid, nitrous products and organic matter as impurities, and the pure or puriss. acids which should not contain the above or other foreign substances.

**1. Fixed Residue.**—10 c.c. are evaporated and calcined in a platinum dish and any residue analysed in the ordinary way, especially for heavy and alkali metals.

**2. Lead, Iron and other Heavy Metals.**—1 vol. of the acid is poured carefully into 5 vols. of 90% alcohol: no heavy, white deposit (*lead sulphate*) should be formed, even after some hours.

5 c.c. are heated with a few drops of nitric acid, allowed to cool, diluted with water and tested with potassium thiocyanate: no red coloration (*iron*) should be observed.

1 c.c., diluted with 20 c.c. of water, should give no brown coloration with hydrogen sulphide (*copper, lead*), and after being made alkaline with ammonia should not become *brown* (*iron*) or turbid (*zinc*).

**3. Arsenic.**—When used in the Marsh apparatus (*see* Flesh Foods, Vol. II) for an hour, the acid should yield no arsenical mirror.

1 c.c., diluted with 2 c.c. of water and treated with 5 c.c. of Bettendorf's reagent (see p. 18), should not become coloured within an hour.

The *quantitative determination* is carried out as follows: 20 grams of the acid are diluted with an equal volume of water and a current of sulphur dioxide passed through the liquid until the latter smells strongly of it. The excess of sulphur dioxide is then expelled by means of carbon dioxide, a little bicarbonate added and the arsenious acid titrated with N/10-iodine and starch paste. 1 c.c. N/10-iodine = 0·00495 gram $As_2O_3$. If iron is present in more than negligible amount, it must be eliminated before applying this method.

**4. Selenium.**—10 c.c. of the acid, diluted with 30 c.c. of water, are treated with 20 c.c. of saturated sulphur dioxide solution: in presence of selenium a reddish-yellow coloration appears, a slight red precipitate being gradually deposited later (if the selenium is not too small in amount).

**5. Ammonia.**—2 c.c. of acid are diluted with about 30 c.c. of water, then rendered alkaline with sodium hydroxide solution and tested with Nessler solution (*see* Potable Waters).

**6. Sulphurous Acid.**—Starch paste is turned blue by a little dilute iodine solution and the acid to be tested diluted and then added to the starch, which is decolorised in presence of sulphurous acid. Or the acid may be diluted, a granule of zinc added and the liquid warmed: evolution of hydrogen sulphide is then tested for by means of lead acetate paper.

**7. Nitrous Compounds, Nitric Acid.**—Ferrous sulphate solution

is poured on to the undiluted acid and the surface of contact of the two liquids examined for a brown ring. Very small quantities of nitrous compounds or of nitric acid may be detected respectively by Griess's reagent (*see* Waters, p. 6) or diphenylamine used as follows: on to a few crystals of pure diphenylamine in a dry test-tube are poured a few c.c. of the acid to be tested and on this as much distilled water so that two layers are formed: the zone of contact of the two layers should show no blue coloration, even after standing.

**8. Hydrochloric Acid.**—The diluted acid is treated with silver nitrate.

**9. Hydrofluoric Acid.**—The acid is warmed in a platinum dish covered with a glass coated with wax which has been scratched so as to uncover the glass in places: if hydrofluoric acid is present, the naked glass is attacked.

**10. Reducing Substances** (*Organic Matter, Sulphurous and Nitrous Acids*).—15 c.c. of the acid are diluted with 45 c.c. of water and a drop of decinormal permanganate solution added: the pink colour should persist for 5 minutes.

**11. Quantitative Determination.**—In absence of other acids, the sulphuric acid may be titrated with N-alkali; 1 c.c. = 0·04904 gram $H_2SO_4$. When other acids are present, precipitation as barium sulphate must be employed.

Crude commercial sulphuric acid always contains arsenic and usually from 0·8 to 4·4 grams per 100 kilos, although as much as 0·5% has been found.

## FUMING SULPHURIC ACID
## (OLEUM)

This is a mixture of the monohydrate ($H_2SO_4$) with sulphuric anhydride and is an oily liquid, rarely colourless but more often brownish; it fumes in the air and is more or less turbid and often partly or completely crystallised. Analysis of this acid includes the determinations described for ordinary sulphuric acid; further, in order to know exactly its value, its content of sulphuric anhydride, monohydrate acid and sulphurous acid, where this is present, must be known. Lunge's method, which is as follows, may be used.

From 3 to 4 grams of the fuming acid, weighed by means of Lunge and Rey's special bulb pipette or any similar instrument and with all the necessary precautions, is dissolved in about half a litre of very cold water and, when the liquid has assumed the air-temperature, the volume made up to 500 c.c. In 100 c.c. of this solution the total acidity is determined by means of N/2–caustic soda solution and methyl orange. In another 100 c.c., any sulphurous acid is determined by N/10–iodine and starch paste. The sulphuric anhydride and monohydrated sulphuric acid are then calculated as follows:

(*a*) *In absence of* $SO_2$: the total acidity is calculated as percentage of $SO_3$; 1 c.c. N/2-NaOH = 0·02003 gram $SO_3$. The sulphuric anhydride thus calculated is then subtracted from 100, the difference representing *the water in* 100 parts of the substance. From the quantity of water thus

found the monohydrate is calculated, 18 parts of water corresponding with 98 of $H_2SO_4$. Finally, subtraction of the percentage of $H_2SO_4$ from 100 gives the free $SO_3$.

(*b*) *In presence of* $SO_2$: in this case the total acidity must be diminished by that due to the sulphurous acid, that is, before calculating the $SO_3$ from the acidity, the number of c.c. of N/10-iodine used in determining the sulphurous acid is divided by 10 and the result subtracted from the number of c.c. of N/2-soda used in the measurement of the acidity [1]; from the number thus obtained the $SO_3$ is calculated as in (*a*). The sum of the $SO_3$ thus found and of the $SO_2$ found directly (1 c.c. N/10-iodine = 0·0032 gram of $SO_2$) is subtracted from 100, the result being the water, from which the $H_2SO_4$ is calculated as in the previous case. Lastly, the $SO_3$ is calculated by subtracting from 100 the sum of the $H_2SO_4$ and the $SO_2$.

Example (of case *b*): 3·422 grams of fuming acid, dissolved in water, were made up to 500 c.c. For 100 c.c. of this solution (= 0·6844 gram of substance) 30·10 c.c. of N/2-caustic soda were required, or 5·25 c.c. of N/10-iodine. Then

$$30{\cdot}10 - 0{\cdot}525 = 29{\cdot}575,$$

so that the $SO_3$ will be

$$29{\cdot}575 \times 0{\cdot}02003 = 0{\cdot}5924,$$

or, allowing for the amount of the fuming acid in 100 c.c.,

$$SO_3 = 86{\cdot}56\%.$$

On the other hand the sulphurous acid will be

$$5{\cdot}25 \times 0{\cdot}0032 = 0{\cdot}0168$$

i.e., $SO_2 = 2{\cdot}46\%$.

Hence the water will be

$$100 - (86{\cdot}56 + 2{\cdot}46) = 10{\cdot}98.$$

To 10·98 of water there correspond 59·78 of $H_2SO_4$, since

$$18 : 98 :: 10{\cdot}98 : 59{\cdot}78.$$

The free $SO_3$ will therefore be

$$100 - (59{\cdot}78 + 2{\cdot}46) = 37{\cdot}76.$$

The acid thus contains

| | |
|---|---|
| $H_2SO_4$ | 59·78% |
| $SO_3$ | 37·76% |
| $SO_2$ | 2·46% |

## TARTARIC ACID

$C_4H_6O_6 = 150$

Large, colourless, transparent, odourless, non-hygroscopic crystals of acid taste, readily soluble in water or alcohol. It may be contaminated especially by small quantities of sulphuric acid or sulphates, salts of calcium, potassium, iron, copper, and particularly lead, and sometimes arsenic. It may be adulterated with cream of tartar, potassium and sodium sulphates, alum and oxalic acid.

The tests to be made are as follows:

**1. Solubility.**—It should dissolve completely in water (absence of calcium tartrate or sulphate).

[1] The reason of this is that, when the acidity is determined in presence of sulphurous acid with methyl orange as indicator, neutrality of the liquid is reached when the acid sulphite, $NaHSO_3$, and not the normal sulphite, $Na_2SO_3$, is formed. Consequently, 1 c.c. of N/10-iodine solution is equivalent, not to 0·1 c.c., but to only 0·05 c.c. of N-soda and therefore to 0·1 c.c. N/2-soda.

**2. Fixed Residue.**—2 grams are cautiously calcined in a platinum dish and any residue examined in the usual way.

**3. Sulphuric Acid.**—The 1 : 10 solution is tested with barium chloride.

**4. Oxalic Acid.**—The 1 : 10 solution, neutralised with ammonia, is treated with calcium sulphate.

**5. Lime.**—The 1 : 10 solution is rendered alkaline with ammonia and tested with ammonium oxalate.

**6. Heavy Metals.**—The 1 : 10 solution is treated with hydrogen sulphide or neutralised with ammonia and then treated with ammonium sulphide.

**7. Arsenic.**—The concentrated solution should not be coloured by Bettendorf's reagent.

**8. Quantitative Determination.**—In absence of other free acids, the aqueous solution of the acid is titrated with N-alkali in presence of phenolphthalein : 1 c.c. N-alkali = 0·07502 gram of tartaric acid.

The pure acid should leave no weighable residue : the Italian Pharmacopœia allows 5 parts per 1000. The commercial acid often contains lead partly combined and partly free ; as much as 0·6 gram per kilo has been found.

## Tartars and other Tartaric Substances

These are mainly *wine lees, cask incrustation, crude tartars* and *crude calcium tartrate.*

*Wine lees* consist of a slimy, reddish mass containing essentially yeasts, cream of tartar, calcium tartrate, colouring matter and water. *Cask incrustations* and *crude tartars* are composed of dirty white or reddish crystalline crusts or masses. *Crude calcium tartrate* is a greyish or reddish powder almost insoluble in water but soluble in dilute acids.

For the analysis of these substances a homogeneous sample must be prepared ; the substance is well mixed and powdered so that it passes through at least a ½ millimetre sieve.

In all the products it is necessary to determine the tartaric acid, whether combined with potash or lime. According to the methods adopted at the Seventh International Congress of Applied Chemistry, London, 1909, the tartaric acid is determined as follows :

**1. Determination of the Tartaric Acid existing as Potassium Bitartrate.**—2·350 grams of the substance are boiled for 5 minutes with about 400 c.c. of water in a 500 c.c. flask, a further quantity of water being added and the whole allowed to cool, made up to volume, mixed and filtered through a pleated filter. Of the filtrate 250 c.c. (= 1·175 gram of substance) are heated to boiling and titrated with N/4-caustic alkali standardised by means of bitartrate (puriss.), using sensitive litmus paper (phenolphthalein may also conveniently be used).

**2. Determination of the Total Tartaric Acid** (Goldenberg and Géromont's method, modified).—6 grams (12, if poor in tartaric acid) of material are weighed and, together with 18 c.c. of HCl (D 1·10), introduced into a 150–200 c.c. beaker. The whole is thoroughly mixed and stirred at the ordinary temperature, the lumps being broken with a glass rod and the particles washed from the sides of the beaker with small quantities of water from a wash-bottle. After digestion for 10–15 minutes, the whole is washed

out into a 200 c.c. flask, made up to volume, mixed and filtered through a dry filter.

By means of a pipette corresponding exactly with the measuring-flask, 100 c.c. of the filtrate (= 3 grams of substance) are introduced into a 300 c.c. beaker already containing 10 c.c. of potassium carbonate solution of density 1·490 (66 grams of anhydrous carbonate in 100 c.c. of solution). After mixing, the liquid is slowly heated and finally boiled for 20–25 minutes until effervescence ceases and the whole of the calcium carbonate thrown down in powder.[1] After cooling to the air-temperature, the liquid and precipitate are poured into a 200 c.c. graduated flask, the beaker being washed repeatedly with distilled water. After making up to volume and mixing, the liquid is filtered through a dry, pleated filter, and 100 c.c. of the filtrate (= 1·5 gram of substance) evaporated on a steam-bath in a 400–500 c.c. porcelain dish until the crystalline skin forming at the edges no longer dissolves on gentle shaking. The evaporation is continued for some minutes with movement of the dish until a dry residue is obtained. This is redissolved in 5 c.c. of boiling water and 4 c.c. of glacial acetic acid then added in drops at the edge of the hot liquid, the whole being stirred vigorously for 5 minutes with a glass rod. After a further interval of 10 minutes, 100 c.c. of 95% alcohol are added and the mixture stirred for 5 minutes to render the precipitate granular and crystalline.

After the lapse of 10 minutes, the alcohol is decanted on to a cellulose filter and drawn through with a pump. The precipitate is washed three or four times with alcohol by decantation, then introduced on to the filter and the washing continued until the alcohol passing through no longer exhibits an acid reaction.

The filter and precipitate are placed again in the dish with 200–300 c.c. of water, boiled for a minute, and titrated in the hot with N/4-potassium hydroxide (standardised with puriss. bitartrate), neutral, sensitive litmus paper being used as indicator. The number of c.c. of alkali used, multiplied by 10 and divided by 4, gives directly the percentage of tartaric acid.

The result obtained must be corrected for the volume occupied in the solutions by the insoluble substances. Where 12 grams of material are taken, the correction is calculated by means of the formula,

$$y = 1 - 0{\cdot}01\ x,$$

where $x$ is the percentage of tartaric acid found and $y$ the amount to be deducted from it ; if 6 grams are taken, the correction is one-half that given by the above formula.

*
* *

*Wine lees* usually contain from 15 to 30% of potassium bitartrate, but sometimes as little as 10% or as as much as 40% ; the Italian products generally contain about 24% of tartaric acid as potassium bitartrate and about 6% as calcium tartrate. *Cask incrustations* contain up to 70–80% of cream of tartar, and *crude tartar* contains more or less according to the method of preparation ;

[1] According to Perciabosco (*Staz. agr. ital.*, 1914, XLVII, p. 803), with material rich in tartrates it is advisable to add the potassium carbonate to the boiling hydrochloric acid solution. In this case the boiling is protracted after the addition of the carbonate for only 10 minutes.

in both products, especially those from plastered wines, variable proportions of calcium tartrate may be found. *Crude calcium tartrate* contains, besides calcium tartrate, small proportions of potassium bitartrate, gypsum, lime, calcium carbonate and organic matter.

## YL (Isoamyl) ALCOHOL

$C_5H_{12}O = 88$

*Crude amyl alcohol* of commerce constitutes *fusel oil*, which contains variable quantities of amyl alcohol (sometimes only 30%) mixed with other higher alcohols, ethyl alcohol, furfural and other impurities. This fusel oil is a more or less yellow liquid of repulsive odour.

*Pure amyl alcohol* of commerce is a colourless or yellowish liquid of peculiar, rather irritating odour, D 0·814–0·816, b.pt. 129–132°, very slightly soluble in water, readily in alcohol, ether or benzene. It almost always contains small proportions of furfural and other impurities. The tests to be made are as follows:

1. **Density, Boiling Point.**—By the ordinary methods.

2. **Residue.**—50 c.c., evaporated on a steam-bath, should leave no appreciable residue.

3. **Furfural, Aldehydes.**—5 c.c., when mixed carefully and with cooling with an equal volume of pure conc. sulphuric acid, should become neither brown nor turbid (a slight reddish or yellowish coloration is permissible). The same result should be obtained with concentrated caustic potash solution.

4. **Alcohol.**—This is detected and determined as in amyl acetate (6).

## ETHYL ALCOHOL

*See* chapter on Spirits and Liqueurs in Vol. II

## METHYL ALCOHOL

$CH_4O = 32$

This is marketed in different qualities: *methyl alcohol puriss.* is a colourless liquid, D 0·796, b.pt. 66°. *Commercial methyl alcohol* (rectified, white methyl alcohol) is a colourless or yellowish liquid, b.pt. usually 64–67°. *Crude methyl alcohol* is a yellowish or brownish liquid with a more or less empyreumatic odour and burning taste, distilling mainly between 60° and 75°.

**Distinctive Tests.**—(*a*) CHARACTERS.—Crude methyl alcohol is distinguished from the rectified alcohol (commercial methyl alcohol)—which is colourless or almost so—by its yellowish or brownish tint, its empyreumatic odour, burning taste and its large content (15–25%) of acetone (for the quantitative determination of acetone, *see* later).

(*b*) REACTION WITH SULPHURIC ACID. To 5 c.c. are added, gradually and with cooling, 5 c.c. of conc. sulphuric acid: pure methyl alcohol assumes only a slightly yellow coloration, whilst the commercial alcohol, whether crude or rectified, gives immediately a brown coloration.

(*c*) PERMANGANATE TEST. 5 c.c. of the alcohol are treated with 1 c.c. of 0·1% permanganate solution. With pure methyl alcohol the pink coloration persists, whereas with the commercial product, either crude or rectified, the permanganate is instantly decolorised.

## *A.* Pure Methyl Alcohol

The tests to be made are as follows:

**1. Sulphuric Acid Test** (*vide supra*).

**2. Permanganate Test** (*vide supra*).

**3. Non-volatile Substances.**—50 c.c. evaporated on a steam-bath should leave no appreciable residue.

**4. Acidity or Alkalinity.**—15–20 c.c. of the alcohol are mixed with an equal volume of water coloured with neutral litmus, the colour of which should not be altered in the mixture.

**5. Solubility in Water.**—15–20 c.c. of the alcohol, mixed with water in any proportion, should give a clear solution.

**6. Solubility in Caustic Soda Solution.**—15–20 c.c. of the alcohol, mixed with concentrated sodium hydroxide solution, should yield a colourless solution (absence of aldehydes).

**7. Distillation.**—50 c.c. of the alcohol, when distilled, should pass over within 0·5° (a 100 c.c. copper flask with side-tube is best).

**8. Acetone.**—1 c.c. of the alcohol is treated with 10 c.c. of 10% sodium hydroxide solution and 5 drops of approximately N/10-solution of iodine in potassium iodide. Even after some time no turbidity, due to iodoform, should be formed (for quantitative determination, *see* later).

**9. Determination of the Methyl Alcohol.**—The content of methyl alcohol is deduced from the specific gravity by means of Klason and Norton's tables (*see* page 40).

## *B.* Commercial Methyl Alcohol, Crude or Rectified

The tests commonly made are:

**1. Acidity or Alkalinity.**—The alcohol is tested with very sensitive litmus paper or, if the product is colourless, with neutral litmus tincture or methyl orange.

**2. Alcoholometric Degree.**—In practice use is made of Gay-Lussac's alcoholometer at 15° or that of Tralles at 15·56°. Although these alcoholometers are graduated for ethyl alcohol, they are used for methyl alcohol, aqueous mixtures of the latter having densities approximating to those of water-ethyl alcohol mixtures.

**3. Distillation.**—This is carried out on 100 c.c., using the flask described for the distillation of pyridine bases (*see* chapter on Tar and its Products), the fractions distilling over for each 5° being collected separately in graduated cylinders.

**4. Solubility in Water.**—10 c.c. are mixed in a 100 c.c. cylinder with 10 c.c. of water and any turbidity noted; 30 c.c. of water are then added, and later further quantities to 100 c.c., any formation of opalescence being observed.

TABLE III

## Specific Gravities of Methyl Alcohol

| Specific Gravity at 15° C. | % of Methyl Alcohol. | | Specific Gravity at 15° C. | % of Methyl Alcohol. | | Specific Gravity at 15° C. | % of Methyl Alcohol. | |
|---|---|---|---|---|---|---|---|---|
| | By Weight. | By Volume. | | By Weight. | By Volume. | | By Weight. | By Volume. |
| 0·7964 | 100·00 | 100·00 | 0·8650 | 74·49 | 80·89 | 0·9350 | 41·79 | 49·01 |
| 0·7975 | 99·64 | 99·77 | 0·8675 | 73·49 | 80·02 | 0·9375 | 40·40 | 47·53 |
| 0·8000 | 98·75 | 99·18 | 0·8700 | 72·48 | 79·13 | 0·9400 | 39·00 | 45·94 |
| 0·8025 | 97·85 | 98·59 | 0·8725 | 71·44 | 78·23 | 0·9425 | 37·54 | 44·29 |
| 0·8050 | 96·96 | 98·01 | 0·8750 | 70·38 | 77·31 | 0·9450 | 36·03 | 42·66 |
| 0·8075 | 96·07 | 97·41 | 0·8775 | 69·31 | 76·39 | 0·9475 | 34·51 | 41·03 |
| 0·8100 | 95·18 | 96·80 | 0·8800 | 68·25 | 75·43 | 0·9500 | 32·95 | 39·35 |
| 0·8125 | 94·28 | 96·18 | 0·8825 | 67·18 | 74·43 | 0·9525 | 31·38 | 37·61 |
| 0·8150 | 93·39 | 95·55 | 0·8850 | 66·09 | 73·41 | 0·9550 | 29·79 | 35·81 |
| 0·8175 | 92·50 | 94·92 | 0·8875 | 64·98 | 72·39 | 0·9575 | 28·14 | 33·89 |
| 0·8200 | 91·60 | 94·28 | 0·8900 | 63·86 | 71·34 | 0·9600 | 26·44 | 31·82 |
| 0·8225 | 90·70 | 93·63 | 0·8925 | 62·76 | 70·28 | 0·9625 | 24·66 | 29·83 |
| 0·8250 | 89·80 | 92·98 | 0·8950 | 61·65 | 69·23 | 0·9650 | 22·89 | 27·83 |
| 0·8275 | 88·88 | 92·31 | 0·8975 | 60·52 | 68·17 | 0·9675 | 21·14 | 25·76 |
| 0·8300 | 87·97 | 91·64 | 0·9000 | 59·36 | 67·09 | 0·9700 | 19·38 | 23·67 |
| 0·8325 | 87·06 | 90·97 | 0·9025 | 58·20 | 65·97 | 0·9725 | 17·63 | 21·54 |
| 0·8350 | 86·16 | 90·29 | 0·9050 | 57·01 | 64·82 | 0·9750 | 15·85 | 19·40 |
| 0·8375 | 85·23 | 89·60 | 0·9075 | 55·82 | 63·65 | 0·9775 | 14·03 | 17·25 |
| 0·8400 | 84·29 | 88·88 | 0·9100 | 54·64 | 62·46 | 0·9800 | 12·27 | 15·12 |
| 0·8425 | 83·34 | 88·13 | 0·9125 | 53·49 | 61·27 | 0·9825 | 10·60 | 13·04 |
| 0·8450 | 82·39 | 87·40 | 0·9150 | 52·31 | 60·04 | 0·9850 | 8·94 | 11·03 |
| 0·8475 | 81·44 | 86·64 | 0·9175 | 51·10 | 58·80 | 0·9875 | 7·32 | 9·06 |
| 0·8500 | 80·47 | 85·88 | 0·9200 | 49·84 | 57·54 | 0·9900 | 5·72 | 7·13 |
| 0·8525 | 79·50 | 85·09 | 0·9225 | 48·54 | 56·20 | 0·9925 | 4·18 | 5·30 |
| 0·8550 | 78·51 | 84·27 | 0·9250 | 47·20 | 54·79 | 0·9950 | 3·01 | 3·84 |
| 0·8575 | 77·50 | 83·44 | 0·9275 | 45·84 | 53·36 | 0·9975 | 1·39 | 1·69 |
| 0·8600 | 76·50 | 82·61 | 0·9300 | 44·49 | 51·92 | 1·0000 | 0·00 | 0·00 |
| 0·8625 | 75·50 | 81·76 | 0·9325 | 43·15 | 50·48 | | | |

**5. Solubility in Caustic Soda Solution.**—20 c.c. of the alcohol are mixed in a 100 c.c. graduated cylinder with 40 c.c. of 32% sodium hydroxide solution (D 1·35) and left for an hour, the volume of the floating insoluble portion being noted.

**6. Determination of the Acetone.**—Messinger's method is used, the following solutions being required:

(*a*) 80 grams of caustic soda (puriss.), free from nitrites, per litre.[1]

(*b*) Approximately 10% sulphuric acid solution, 100 grams of the pure conc. acid being made up to a litre; 10 c.c. of this solution should more than neutralise 10 c.c. of (*a*).

(*c*) Approximately N/5-iodine solution, obtained by dissolving about

[1] 10 c.c. of this solution, treated with 0·1–0·2 gram of potassium iodide and acidified with hydrochloric acid, should yield no free iodine.

25·5 grams of iodine in a solution of 50 grams of potassium iodide in 200 c.c. of water and making the volume up to 1 litre.

(*d*) Approximately N/10-sodium thiosulphate solution, prepared by dissolving 25 grams of the pure salt to 1 litre.

(*e*) Fresh starch paste.

TITRATION OF THE THIOSULPHATE SOLUTION. To 20 c.c. of an aqueous solution containing 3·863 grams of potassum dichromate per litre are added 10 c.c. of 10% potassium iodide solution and 5 c.c. of hydrochloric acid (D 1·10). After mixing, 100–150 c.c. of water are added and the free iodine titrated with the thiosulphate solution. Towards the end of the titration, a little starch paste is added, addition of the thiosulphate being discontinued when a drop of the latter changes the greenish blue colour to pale green. Since 20 c.c. of the dichromate solution set free 0·2 gram of iodine from the potassium iodide, the amount of iodine corresponding with 1 c.c. of the thiosulphate solution may be readily calculated.

TITRATION OF THE IODINE SOLUTION. 10 c.c. of the iodine solution are pipetted into a dish and the thiosulphate solution run in from a burette until the liquid becomes pale yellow. Starch paste is then added and the titration continued until the liquid becomes colourless. The amount of iodine in 10 c.c. of the solution is found by multiplying the number of c.c. of thiosulphate used by its iodine equivalent.

METHOD OF WORKING. 25 c.c. of the alcohol [1] are introduced into a litre flask containing about 500 c.c. of water and the solution made up to volume. After mixing, 10 c.c. of the liquid (corresponding with 0·25 c.c. of the methyl alcohol) are placed in a 300–400 c.c. bottle fitted with a ground stopper and containing 10 c.c. of the caustic soda solution (*a*); after mixing, 40 c.c. of solution (*c*) are added from a burette. The closed bottle is left for an hour with occasional shaking, after which 10 c.c. of solution (*b*) are added and the non-combined iodine titrated with the sodium thiosulphate solution (*d*). Subtraction of non-combined iodine from the amount contained in 40 c.c. of the iodine solution gives the amount reacting.[2] If the latter is *a* grams, the percentage of acetone is given by the formula,

$$\frac{58{\cdot}05 \times a}{761{\cdot}52} \times 100.$$

This gives the number of grams of acetone in 100 c.c. of the methyl alcohol; multiplication by 0·7966—the density of acetone at 15°—then yields the percentage of acetone by volume.

**7. Bromine Absorption.**—From this determination the quantity of various impurities, principally allyl alcohol, is deduced. The reagents required are:

(*a*) A solution of potassium bromate and bromide, prepared thus: Powdered potassium bromate and bromide (puriss.) are dried separately in porcelain dishes for 2 hours at 100°. 2·447 grams of the bromate and

[1] With rectified methyl alcohol, 50–100 c.c. are taken according to its supposed acetone content.

[2] Each mol. of acetone (58·05) requires 6 atoms of iodine (761·52).

8·719 grams of the bromide are dissolved separately in water and the two solutions mixed and made up to 1 litre.

(*b*) 1 volume of conc. sulphuric acid, mixed with 3 vols. of water and cooled.

The procedure is as follows: 100 c.c. of solution (*a*) and 20 c.c. of solution (*b*) are mixed in a 100 c.c. flask and the methyl alcohol run in slowly from a burette until the liquid appears colourless, the determination being made in daylight and not in artificial light. The bromine absorption is expressed by indicating the number of c.c. of methyl alcohol used.

**8. Esters.**—To 10 c.c. of the methyl alcohol mixed with 40 c.c. of water and a few drops of phenolphthalein solution N/10-potassium hydroxide solution is added until the liquid becomes pale pink. The liquid is then boiled for 15 minutes with 20 c.c. of N-caustic soda solution and, after cooling, the excess of alkali is titrated with N-sulphuric acid. Multiplication of the number of c.c. of caustic potash absorbed in the saponification by 0·74 gives the quantity of esters, calculated as methyl acetate, in 100 c.c. of the alcohol.

***

*Methyl alcohol* (*puriss.*) is a colourless, neutral liquid, with a pleasant odour recalling that of ethyl alcohol, and shows at least 99° on the alcoholometer and contains not more than 0·1% of acetone. It should distil within 0·5° and the sulphuric acid test should give only a slightly yellow liquid. It should not decolorise permanganate immediately and should mix in all proportions with water without opalescence and should mix with concentrated caustic soda solution without becoming coloured.

*Commercial methyl alcohol* (rectified, white methyl alcohol) is colourless or only faintly yellowish, with a distinctive, stinging odour (not empyreumatic); its alcoholometric strength is 95–99°, its b.pt. 64–67°, and as a rule it contains 1–3% of acetone (some qualities used as solvents contain as much as 15-20%).

*Crude methyl alcohol* or *wood spirit* is a yellowish liquid of empyreumatic odour and burning taste, its alcoholometric strength being 90–91°; it is not completely soluble in caustic soda solution (15–20% separates), contains 15–25% of acetone and distils to the extent of 90% between 60° and 75°. The impurities are principally acetone, methyl acetate, allyl alcohol, ammonia and pyridine bases, empyreumatic products, etc.

Crude methyl alcohol to be used for the denaturation of alcohol must satisfy, in different countries, definite conditions as to colour, specific gravity, boiling point, solubility in water and in caustic soda solution, acetone content, absorption of bromine and other less important characters.

## ALUM—POTASSIUM ALUMINIUM SULPHATE

$Al_2(SO_4)_3$, $K_2SO_4 + 24H_2O = 949{\cdot}2$

Large, colourless, transparent crystals, which slowly effloresce in the air, soluble in 10 parts of water, insoluble in alcohol. It is usually moderately pure and it is usually sufficient to test it for iron and free sulphuric acid, as described under Aluminium Sulphate.

## ALUMINIUM ACETATE

For use in dyeing, *normal aluminium acetate*, $Al(C_2H_3O_2)_3$, the *basic acetate* and various *sulpho-acetates* are sold, mostly in solution.

The impurities to be sought in these products are lead, zinc, iron, lime

and alkali, which are detected and determined as in aluminium sulphate (*vide infra*). The value depends on the content of alumina, acetic acid and sulphuric acid: the alumina and sulphuric acid are determined as in aluminium sulphate and the acetic acid as in calcium acetate (*q.v.*).

The compositions of the basic acetates and sulpho-acetates of aluminium vary considerably. The sulpho-acetate should preferably contain 1 part of $SO_3$ per 2 parts of $Al_2O_3$.

The various aluminium acetates should be free more especially from iron and zinc (*see also* Aluminium Sulphate).

## ALUMINIUM SULPHATE

$$Al_2(SO_4)_3 + 18H_2O = 666{\cdot}2$$

This exists in commerce in various forms: white, crystalline, nacreous scales; in lumps or cubical or prismatic cakes, which are hard, white and opaque; in spongy, anhydrous, white masses. In the first two forms it is easily and completely soluble in water giving an acid solution; the anhydrous form dissolves slowly and often leaves an insoluble residue of basic sulphate.

The most frequent impurities are small quantities of iron salts and free sulphuric acid (to be tested for more especially when the product is to serve for dyeing purposes), insoluble substances (silica, sand) and rarely zinc, copper, lead, chromium, titanium and arsenic.

Analysis consists essentially of determinations of the insoluble matter, alumina, free and total sulphuric acid and iron and is carried out as described below. Tests for the other impurities mentioned above are made by the ordinary methods.

The sample to be analysed is powdered rapidly and weighed in a closed vessel.

**1. Insoluble Matter.**—A solution of 20 grams in water is filtered through a filter previously dried at 105° and weighed. The insoluble matter is thoroughly washed, dried at 105° and weighed. The filtrate is made up to 500 c.c. and used for the following determinations.

**2. Alumina.**—This is determined in 50 c.c. of the solution (2 grams of material) by precipitating with ammonia and weighing as $Al_2O_3$ [1]; the weight found is diminished by that of the $Fe_2O_3$ found as in 5 (below).

**3. Total Sulphuric Acid.**—This is determined in 25 c.c. of the solution (1 gram of material) as barium sulphate. 1 part of $BaSO_4 = 0{\cdot}34335$ part of $SO_3 = 0{\cdot}4206$ part of $H_2SO_4$. From the result is deducted any free acid found (4).

From the relation between the alumina and the sulphuric acid is calculated the *basicity* of the product, from which it is deduced whether the sulphate is normal or more or less basic. By *basicity number* is meant the

[1] In order to avoid the action of organic substances, which may occur in the commercial sulphate, Delage (*Ann. de chim. analyt.*, 1911, p. 325) recommends the addition of a few drops of bromine to the solution, which is then evaporated to dryness, heated slightly until the residue is completely decolorised, then taken up in water and precipitated with ammonia.

quotient obtained by dividing the percentage of sulphuric acid ($H_2SO_4$) by that of aluminium (Al).

**4. Free Sulphuric Acid.**—According to Iwanow,[1] 25 c.c. of the solution (1 gram of substance) are heated to about 85° with 25 c.c. of water in a 100 c.c. flask, and to the hot liquid are added, with continual shaking, 12 c.c. of a 1 : 12 potassium ferrocyanide solution and then 20 c.c. of 1 : 10 barium chloride solution. After vigorous shaking, the liquid is made up to volume, 0·25 c.c. of water being added to compensate for the volume occupied by the precipitate ; after standing, 25 or 50 c.c. of the clear liquid are titrated with N/10-alkali in presence of methyl orange [2] ; 1 c.c. N/10-alkali = 0·0049 gram $H_2SO_4$.

**5. Iron** (Lunge and Kéler's colorimetric method).—The following are required :

(*a*) 10% potassium thiocyanate solution ;

(*b*) pure ether ;

(*c*) 8·634 grams of ferric ammonium sulphate (iron alum) and 6 c.c. of pure conc. sulphuric acid per litre ; 1 c.c. of this solution diluted to 100 c.c. gives a solution containing 0·010 gram of iron per litre ;

(*d*) pure nitric acid, free from iron ;

(*e*) cylinders with ground stoppers and of exactly equal height and diameter (internal and external), reading from 0 to 25 c.c. in tenths and having a space of at least 5 c.c. between the 25 c.c. mark and the stopper.

The procedure is as follows : 25 c.c. of the solution of the sulphate prepared as in (1) (= 1 gram of substance) are evaporated on a steam-bath to about 5 c.c., 1 c.c. of nitric acid (*d*) being then added and the liquid heated for a few minutes, allowed to cool and diluted to 50 c.c. (solution *S*) ; further 1 c.c. of the same nitric acid is diluted to 50 c.c. (solution *N*). Into one cylinder (*A*) are poured 5 c.c. of solution *S*, and into another (*B*) 5 c.c. of solution *N* to which is added a measured volume (say, 1 c.c.) of the diluted ferric solution *c* (= 0·00001 gram Fe), the liquids in the two cylinders being made up to the same volume with water. To each cylinder are then added 5 c.c. of thiocyanate solution *a* and 10c. c. of ether, the cylinders being next closed and shaken until the aqueous layers are decolorised. A comparison is then made of the intensity of colour of the ethereal layers in the two cylinders (if the coloration is light, the comparison is made after some hours of rest). This process is repeated with different volumes of the iron alum solution until the colours of the two ethereal layers match exactly ; 0·1 c.c. of the ferric solution should produce an appreciable difference in colour intensity.

This process is applicable to sulphates containing less than 0·25% Fe ; with larger proportions, a more dilute solution must be used.

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Pure aluminium sulphate, $Al_2(SO_4)_3 + 18H_2O$, contains 15·33% of $Al_2O_3$

[1] *Chem. Zeit.*, 1913, pp. 805 and 814.

[2] The ferrocyanide precipitates all the aluminium salt and the free sulphuric acid remains in the solution ; the barium chloride then precipitates the excess of ferrocyanide and the free sulphuric acid, but liberates hydrochloric acid equivalent to the latter.

or 8·13% Al, 44·4% $H_2SO_4$ and 48·64% of water, its index of basicity being 5·45. With the simple basic sulphate, $Al_2(SO_4)_2(OH)_2$, the index of basicity is 3·62 and with $Al_2(SO_4)(OH)_4$, 1·81.

Commercial sulphates of good quality should not contain more than 1% of insoluble matter, and their content of iron is usually very small (0·0002–0·005%). For turkey-red dyeing their iron content should not exceed 0·001%, whilst for cotton printing as much as 0·05% is allowed.

The free sulphuric acid varies usually from 0·2 to 1% and is, of course, absent from the basic sulphates. The presence of zinc is always harmful, but it is seldom found.

## AMMONIA

$NH_3 = 17·03$ (17)

Ammonia is commonly sold in aqueous solution, D = 0·910, containing 25% by weight of $NH_3$; the strongest solution, D=0·880, contains about 35·8 % $NH_3$. The pure solution is colourless and has a pure ammonia smell, whereas the technical product may be yellowish and has a more or less pronounced empyreumatic odour.

*Liquefied ammonia* is also sold and is prepared by liquefying the gas in steel cylinders. It contains 97–99% of $NH_3$, besides water, traces of ammonium salts and lubricating oil from the compressor.

The commonest impurities of ammonia solution consist of chlorides, sulphates, carbonates, copper, lead, iron, zinc, lime, pyridine bases and tarry products, which are detected as below. The ammonia content is determined as in 5.

**1. Chlorides, Sulphates.**—10–20 c.c., rendered acid with dilute nitric acid, should not be rendered turbid by silver nitrate (chlorides) or by barium chloride, even after 12 hours (sulphates).

**2. Carbonates.**—10 c.c., mixed with 30 c.c. of lime water, should not become turbid.

**3. Metals.**—10 c.c., diluted with 40 c.c. of water, should not be rendered coloured or turbid by hydrogen sulphide (copper, lead, iron, zinc) or ammonium oxalate (calcium).

20 c.c. should leave no appreciable residue on evaporation.

**4. Pyridine Bases, Tarry Products.**—These may be detected by the smell, especially after exact neutralisation of the ammonia with dilute sulphuric acid.

10 c.c., rendered acid with 20 c.c. of pure 1 : 3 sulphuric acid (which does not decolorise permanganate), should be persistently coloured by 1 drop of decinormal permanganate.

2 c.c., added to 4 c.c. of nitric acid, should give a colourless liquid leaving a white residue on evaporation on a steam-bath.

**5. Quantitative Determination of the $NH_3$.**—The proportion of ammonia in the solution may be found from the specific gravity or by titration with a normal acid in presence of methyl orange (1 c.c. N-acid = 0·017 gram $NH_3$).

## AMMONIUM CARBONATE

The commercial product must be regarded as a mixture of ammonium bicarbonate and carbamate, $NH_4HCO_3 + NH_4 \cdot CO_2 \cdot NH_2 = 157$ (32·5% $NH_3$). It forms white, fibrous, crystalline masses, emitting an odour of ammonia and is slowly soluble in 4–5 parts of water at the ordinary temperature.

It may contain small quantities of chlorides, sulphates, tarry matters and fixed substances.

**1. Chlorides, Sulphates.**—A solution of 1 gram in 10 c.c. of dilute nitric acid should not be rendered turbid by silver nitrate or barium chloride.

**2. Tarry Matters.**—2 grams should give a colourless solution with nitric acid and the solution leave a white residue on evaporation.

**3. Volatility.**—10 grams should leave no appreciable residue when heated.

**4. Determination of the Ammonia.**—This is made by distillation as described for fertilisers or by direct titration of a solution of the carbonate with a normal acid in presence of methyl orange; 1 c.c. N-acid = 0·017 gram $NH_3$.

Commercial ammonium carbonate contains about 31% $NH_3$.

## AMMONIUM CHLORIDE

$NH_4Cl = 53{\cdot}47$ (53·5)

This is put on the market in lumps or crystalline powder, the pure being white and that for industrial purposes grey or yellowish. It may contain as impurities, sulphates, phosphates, thiocyanates, iron, lead, and empyreumatic matters.

**1. Volatility.**—10 grams are heated until all white fumes disappear, any residue being tested for heavy metals, alkalies and alkaline earths.

**2. Sulphates.**—The 1 : 10 solution is treated with barium chloride.

**3. Phosphates.**—4 grams, dissolved in 40 c.c. of 5% magnesium chloride solution and treated with 6 c.c. of ammonia, should not become turbid, even after 12 hours.

**4. Thiocyanates.**—The 1 : 10 solution, acidified with hydrochloric acid, is tested with ferric chloride.

**5. Iron.**—The 1 : 10 solution, acidified with hydrochloric acid, is tested with potassium ferrocyanide. Quantitative determination may be carried out as in aluminium sulphate (*q.v.*).

**6. Empyreumatic and Tarry Matters.**—2 grams, moistened with a little nitric acid, are heated to dryness on a steam-bath: in presence of tarry products a yellowish residue remains, the residue otherwise being white.

**7. Quantitative Determination.**—The chlorine is estimated volumetrically by Volhard's method (*see* Potable Waters) and the ammonia by *distillation* with sodium hydroxide (*see* Fertilisers).

## AMMONIUM PERSULPHATE

$NH_4SO_4 = 114$

Colourless crystals, alterable in moist air, soluble in water. The aqueous solution decomposes slowly with evolution of oxygen, and rapidly when heated with an acid; it decomposes potassium iodide solution, liberating iodine. It always contains more or less marked quantities of ammonium bisulphate, moisture, and alkali, its value depending on its content of the persulphate.

**1. Determination of the Persulphate** (Ulzer's method).—0·3 gram is dissolved in about 100 c.c. of water in a flask with a stopper fitted with a Bunsen valve and the liquid boiled for about 30 minutes with excess of ferrous ammonium sulphate (1–1·5 gram) and dilute sulphuric acid. The excess of ferrous salt is then titrated with standard permanganate (1 c.c. N/10-permanganate = 0·0114 gram of $NH_4SO_4$).

The persulphate may also be determined iodometrically. According to Mondolfo, 2–3 grams of the persulphate are dissolved in 100 c.c. of cold water and 10 c.c. of the solution heated for 10 minutes in an oven at 60–80° with an excess (0·25–0·5 gram) of potassium iodide (puriss.) in a small bottle with a ground stopper. The iodine liberated is titrated with N/10-thiosulphate and starch paste (1 c.c. N/10-thiosulphate = 0·0114 gram $NH_4SO_4$).

From the amount of persulphate present, the active oxygen which a commercial persulphate can furnish may be calculated, knowing that 1 part of $NH_4SO_4 = 0·07$ part of oxygen.

**2. Other Determinations.**—Complete analysis includes determinations of: (*a*) the total sulphuric acid, by precipitation with barium chloride after the persulphate solution has been boiled with hydrochloric acid until the persulphate is completely decomposed; (*b*) the total ammonia, by one of the ordinary methods (*see* Fertilisers); (*c*) the acidity, by titrating a solution of the persulphate, made in the cold, with N-alkali and methyl orange; (*d*) the fixed residue after calcination. From the total sulphuric acid is subtracted that combined with the ammonia as persulphate (1) and from the total ammonia that in the form of persulphate; if sulphuric acid and ammonia remain, they are regarded as existing as ammonium bisulphate.

In the same way *potassium persulphate*, $KSO_4 = 135·1$, is analysed.

## AMMONIUM SULPHATE

(*See* Fertilisers)

## AMMONIUM THIOCYANATE

## (Ammonium Sulphocyanide)

$NH_4CSN = 76$

Colourless, deliquescent crystals, extremely soluble in water or alcohol. Its analysis includes tests for certain impurities (sulphates, iron, lead) and determinations of the proportions of thiocyanic acid and ammonia.

**1. Solubility.**—1 gram should give a clear solution with 10 c.c. of absolute alcohol.

**2. Volatility.**—2 grams should volatilise without leaving appreciable residue when heated in a platinum crucible.

**3. Sulphates.**—The 1 : 20 solution, when treated with barium chloride solution, should remain clear at least 5 minutes.

**4. Metals.**—The 1 : 20 solution should not change with ammonium sulphide (*lead, iron,* etc.) and, when acidified with dilute hydrochloric acid, should remain colourless (iron).

**5. Thiocyanic Acid.**—10 grams are dissolved in water and the solution made up to 500 c.c. To 5 c.c. of the solution (= 0·1 gram of substance) are added 20 c.c. of N/10-silver nitrate, the liquid being acidified with nitric acid and a few drops of saturated ferric alum solution added; the excess of silver nitrate is then titrated with N/10-potassium thiocyanate solution until a reddish coloration appears. The difference between the 20 c.c. of silver nitrate and the number of c.c. of thiocyanate, multiplied by 5·9, gives percentage of HCNS, and multiplied by 5·8, percentage of CNS.

**6. Ammonia.**—This is determined by distillation (*see* Fertilisers) with magnesium oxide instead of sodium hydroxide.

Chemically pure ammonium thiocyanate contains 77·63% of HCNS and 22·37% of $NH_3$; the commercial pure product, which should be perfectly white and odourless, almost always contains traces of lead, iron, and moisture. It occurs also in a yellowish form with an empyreumatic odour and contaminated with marked proportions of sulphate.

## AMMONIUM VANADATE

$NH_4VO_3 = 117$

White or faintly yellow crystalline powder, soluble in water. The purity and value are deduced from the determination of the vanadic acid.

**Determination of the Vanadic Acid.**—1–2 grams, dissolved in very little water, are treated in the hot with excess of saturated ammonium chloride solution, in which ammonium vanadate is insoluble; after 48 hours, the liquid is filtered and the precipitate washed with saturated ammonium chloride solution and then with about 50% alcohol. After being dried at 100°, the precipitate is detached as well as possible from the filter, the latter being burned separately, its ash moistened with nitric acid and again calcined; the precipitate is then added and the whole calcined and the vanadic anhydride weighed. 1 part $V_2O_5$ = 1·286 part $NH_4VO_3$.

## AMYL ACETATE

$C_5H_{11}\cdot C_2H_3O_2 = 130$

Colourless, neutral liquid of pleasant, ethereal odour, D = 0·875 at 15°, b.pt. 138–139°, very slightly soluble in water but readily in alcohol or ether. It may be contaminated with amyl, ethyl, propyl and butyl alcohols and their acetic esters and by acetic, sulphuric and hydrochloric

acids. It is adulterated with ethyl acetate, acetone, benzene and mineral oils. Its analysis includes the following tests and determinations.[1]

**1. Specific Gravity.**—This is measured by Mohr's balance or the picnometer at 15°. The presence of amyl, ethyl, propyl alcohols, etc., acetone or mineral oil lowers the specific gravity, whilst that of ethyl, or propyl acetate, etc., or benzene raises it.

**2. Boiling Point.**—100 c.c. are distilled from a flask furnished with a thermometer, the different fractions distilling up to 100°, 100–110°, etc., being collected. With the exception of the mineral oils (150–170°), the various impurities and adulterants mostly boil at lower temperatures than pure amyl acetate (138°).

**3. Non-volatile Substances.**—20 c.c. are evaporated slowly on a steam-bath and any weighable residue determined. Further, a drop is evaporated on a filter-paper and any residual oily spot observed.

**4. Solubility.**—1 c.c. is shaken with an equal volume of benzene or carbon disulphide or with 10 c.c. of 90% alcohol and 10 c.c. of water and note taken if a limpid solution is formed with each of these solvents.

**5. Free Acids.**—10 c.c. are shaken with as much water and, after standing, the aqueous liquid separated and tested with litmus paper; or the aqueous solution is acidified with dilute nitric acid and tested with barium chloride (*sulphuric acid*) and with silver nitrate (*hydrochloric acid*).

**6. Alcohol and Acetone.**—10 c.c. are shaken with an equal volume of saturated calcium chloride and, after standing, any diminution in the volume of the acetate observed (in a graduated cylinder any diminution may be measured approximately). The aqueous liquid is separated and distilled, the distillate being tested for ethyl alcohol (*see* Amyl Alcohol) and acetone (*see* Methyl Alcohol).

If the *proportion of ethyl alcohol* is required, 50 c.c. of the amyl acetate are shaken with 100 c.c. of calcium chloride solution of D = 1·25 and 30 c.c. of pure cumene. After standing, the aqueous liquid is separated and the supernatant amylic liquid treated with two further quantities of 50 c.c. of the calcium chloride solution. The aqueous liquids are then united and distilled until 50 c.c. is collected, this being filtered through a dry paper and the alcohol content determined by means of the specific gravity. It is, of course, necessary that the product examined shall be free from acetone and other liquids soluble in water.

**7. Ethyl Acetate.**—10 c.c. are boiled for 30 minutes in a reflux apparatus with 50 c.c. of a 15% solution of potassium hydroxide in amyl alcohol. The liquid is then distilled and the first 1–2 c.c. collected shaken with water and the aqueous liquid tested for ethyl alcohol.

For the *quantitative determination*, 50 c.c. of the substance and 25–30 grams of caustic potash dissolved in 50 c.c. of amyl alcohol are taken and 50 c.c. distilled over. The distillate is then treated as indicated in section 6 for the determination of the alcohol. The alcohol by volume multiplied by 1·508 gives the weight of ethyl acetate in 100 c.c. of the amyl acetate tested.

[1] For the analysis of amyl acetate see also article by Chercheffski in *Les matières grasses*, 1913, p. 3103.

**8. Benzene and Mineral Oils.**—2–3 c.c. are shaken in a test-tube with as much pure sulphuric acid (66° Baumé); after 5–10 minutes the appearance of a turbidity indicates *benzene* or the separation at the surface of drops or a liquid layer, *mineral oils*.

**9. Determination of the Amyl Acetate.**—This is effected by means of the saponification number, proceeding as with essential oils (*q.v.*). The saponification number of pure amyl acetate is 431; 1 part of KOH = 2·3169 parts of $C_5H_{11}\cdot C_2H_3O_2$.

Ethyl, propyl and butyl acetates, having the respective saponification indices, 636, 549 and 483, raise that of amyl acetate, whilst alcohols (amyl, ethyl), acetone, benzene and mineral oils lower it.

Commercial amyl acetate almost always contains a certain proportion of free amyl alcohol. It may be regarded as technically pure (e.g., when required for photometric purposes) when it has D = 0·872 – 0·876, distils to the extent of 90% between 137° and 143°, has a saponification number of about 430, is neutral and leaves no oily spot on filter-paper.

## ANILINE

$C_6H_5\cdot NH_2 = 93$

Various qualities of aniline are found on the market: *Pure aniline* (*aniline oil for blue*), a colourless or yellowish liquid which readily turns brown in the air and light, and has an aromatic odour. *Aniline oils* (*crude anilines*), mixtures of aniline with ortho- and para-toluidines, form reddish-brown liquids of unpleasant odour. *Aniline oil for red* contains about equal proportions of aniline, ortho- and para-toluidine, and *aniline oil for safranine* about 40% of aniline and 60% of orthotoluidine. *Liquid toluidine* is a mixture of ortho- and para-toluidines with a little aniline.

### 1. Aniline

With aniline, besides determinations of the specific gravity and boiling point by the ordinary methods, the following tests are made:

**1. Non-basic Substances.**—10 c.c. should give a quite clear solution with 50 c.c. of water and 40 c.c. of hydrochloric acid; incomplete solution indicates the presence of hydrocarbons and nitrobenzene.

**2. Moisture.**—100 c.c. are distilled, the first 10 c.c. of distillate being collected in a graduated 15 c.c. cylinder and shaken with 1 c.c. of saturated sodium chloride solution and any diminution in its volume noted.

**3. Sulphur.**—100 c.c. are boiled for some time in a reflux apparatus (the sulphur being transformed into hydrogen sulphide) and a current of carbon dioxide then passed through the aniline into silver nitrate solution; a black precipitate in the latter indicates that the aniline contains sulphur. This test is quantitative when standard silver nitrate solution is used and the titre determined after removal of the sulphide by filtration.

**4. Determination of the Aniline.**—If the preceding tests indicate that the aniline is not pure, the aniline may be determined by the method described below for aniline oils.

*Pure aniline has* D 1·0267 at 15° and b.pt. 184°. The commercial pure pro-

duct should have D 1·0265–1·0267 and from 87 to 98% of it should distil within 1–1·5°; it should contain only traces of moisture and impurities.

## 2. Aniline Oils

With aniline oils, besides the above determinations, the proportions of the various bases present, namely, aniline and o- and p-toluidines are determined. The estimation may be made by Reinhardt's method,[1] which is based on the fact that, with a mixture of potassium bromide and bromate, aniline in acid solution is transformed into tribromoaniline, whereas o- and p-toluidines give dibromo-compounds, and that by oxalic acid in acid solution, p-toluidine and aniline are precipitated whilst o-toluidine remains in solution. The procedure is as follows:

(*a*) DETERMINATION OF THE ANILINE AND OF THE TWO TOLUIDINES TOGETHER. The brominating mixture is prepared from 490 grams of bromine, 336 of caustic potash and 1 litre of water; the liquid is boiled gently for 2–3 hours and diluted to 9 litres (it should be free from hypobromite).[2] To 1·5–2 grams of pure aniline are added 100 c.c. of hydrobromic acid of D = 1·45–1·48 (or the corresponding quantities of KBr and HCl), the liquid being diluted with a litre of water and the above brominating solution added from a burette until a drop of the liquid colours a starch-iodide paper blue. Division of the amount of aniline taken by the number of c.c. of the brominating solution required gives the quantity of aniline (*t*) corresponding with each c.c. of the brominating solution.[3] From 1· to 2 grams of the aniline oil are then titrated in the same way, the content in aniline (*x*) being calculated from the formulæ:

$$x = 2{\cdot}3777\ v\ t - 1{\cdot}3777\ a,$$

so that the percentage (*p*) of aniline will be

$$p = \frac{x\ .100}{a},$$

where $a$ = quantity of substance taken.
$x$ = aniline content in $a$.
$v$ = c.c. of brominating solution used in test.
$t$ = titre in aniline of the brominating solution.

The percentage of the two toluidines together in the oil will be

$$100 - p.$$

(*b*) DETERMINATION OF P-TOLUIDINE WHEN MIXED WITH EITHER ANILINE OR O-TOLUIDINE OR WITH BOTH BASES. 100 grams of the oil are dissolved in 106 grams of 31% hydrochloric acid (D 1·163) and the liquid poured into a boiling 10% solution of pure oxalic acid;[4] the liquid should remain

[1] *Chem. Zeit.*, 1893, p. 413.

[2] An approximately N/7-solution of recrystallised potassium bromate may also be used.

[3] This titre remains moderately constant.

[4] The quantity of oxalic acid should be greater than that necessary to precipitate all the p-toluidine present, which may be established by a preliminary experiment. For oils poor in aniline, about 10 grams of oxalic acid more than is necessary should be used, and for those richer about 20 grams more. In general, 50 grams of oxalic acid in 500 c.c. of water may be used for 100 grams of oil.

clear. During cooling the liquid is frequently shaken and after standing for 48 hours is filtered to separate the oxalates, which are washed with 3 quantities of 25 c.c. of water and are then treated with boiling potassium hydroxide solution (100 c.c. of potassium hydroxide solution of 45° Baumé and 200 c.c. of water). In this way the oxalates are decomposed, and after cooling the bases (aniline and p-toluidine) are separated and weighed, the o-toluidine being then determined by difference. If the aniline is determined, as in (*a*), in the mixture of bases separated from the oxalates and dried with potash, the proportion of aniline and hence that of p-toluidine in the oil are known.

Aniline oil for red has D = 1·006–1·009 at 15°, distils almost completely between 182° and 198° and is almost entirely soluble in dilute hydrochloric acid. That for safranine has D = 1·032 – 1·034 and often contains considerable quantities of non-basic products, so that it gives a very turbid solution with dilute hydrochloric acid ; it contains as a rule 4–6% and sometimes 12% of p-toluidine.

### 3. Liquid Toluidine

The determinations to be made are the same as with aniline oils. According to Lunge [1] the density may be used to deduce the proportions of o- and p-toluidines, when aniline and other substances are absent.

o- and p-Toluidines are also sold in a fairly pure form. The former is a liquid, D = 1·0037 at 15°, b.pt. 198° and the second solid, D = 1·046, m.pt. 45°, b.pt. 198°.

## ANTIMONY AND POTASSIUM TARTRATE

## (Tartar Emetic)

$$K(SbO)C_4H_4O_6 + \tfrac{1}{2}H_2O = 332{\cdot}3$$

Colourless, transparent crystals, which readily effloresce, becoming opaque, irregular pieces or crystalline powder. It dissolves in 17 parts of cold water with a faintly acid reaction, but is insoluble in alcohol. It may be impure with cream of tartar, calcium salts, sulphates, chlorides, antimony and potassium oxalate, iron, zinc, copper, lead and arsenic. The various tests to be made are as follows :

**1. Solubility.**—A clear solution should be obtained with 0·5 gram and 8–10 c.c. of cold water or 1 c.c. of boiling water ; any insoluble residue indicates cream of tartar or calcium salts.

**2. Sulphates, Chlorides, Oxalates, Lime.**—4 grams are dissolved in 80 c.c. of water acidified with tartaric acid and four portions of the solution tested respectively with barium chloride, silver nitrate, calcium chloride and ammonium oxalate.

**3. Arsenic.**—0·5 gram, dissolved in a little conc. hydrochloric acid and treated with 5 c.c. of Bettendorf's reagent, should not colour within an hour.

**4. Metals.**—1 gram, dissolved in 20 c.c. of water and sodium hydroxide solution added until the precipitate formed redissolves and then saturated

[1] *Chem. Ind.*, 1885, VIII, p. 74.

with hydrogen sulphide, should not give a brown (*iron, copper, lead*) or white turbidity (*zinc*).

**5. Determination of the Antimony.**—0·5 gram is dissolved in 50 c.c. of water and 10% sodium bicarbonate solution added to give an alkaline reaction; should a little precipitate form, it is removed by addition of a little Rochelle salt dissolved in water. Starch paste is added and the liquid titrated with N/10-iodine until a blue colour, persisting for a short time, is obtained. 1 c.c. N/10-iodine = 0·00721 gram $Sb_2O_3$ = 0·00601 gram Sb.

* * *

Chemically pure tartar emetic contains 43·4% $Sb_2O_3$, and the commercial products usually contain 42–43%. For use in dyeing it should be free especially from iron, whilst for medicinal purposes it should contain none of the above impurities and should hence answer all the tests 1–4.

As substitutes for tartar emetic in dyeing, various other antimony compounds are used, such as *double oxalates and fluorides of antimony and potassium or sodium and ammonium*, or *lactates of antimony and sodium or calcium* (*antimonin*). In these products the antimony is determined as in 5 (above), and the test for iron made.

## BARIUM CHLORIDE

$BaCl_2 + 2H_2O = 244·29$

Colourless crystals, soluble in water, insoluble in conc. hydrochloric acid. The commercial salt for technical uses may be yellowish or greyish and in fine powder (flour).

It may contain, as impurities, iron, calcium chloride (hygroscopic) and potassium chloride (sometimes large quantities). In general, the following tests are sufficient:

**1. Solubility, Heavy Metals.**—1 gram, dissolved in 10 c.c. of water, should give a clear, neutral solution which, when acidified with hydrochloric acid, is not altered by potassium ferrocyanide (*iron*) or hydrogen sulphide, even after being made alkaline with ammonia (*other metals*).

**2. Lime and Alkalies.**—5 grams, dissolved in 50 c.c. of water, are precipitated in the hot by dilute sulphuric acid and filtered: the filtrate should not be rendered turbid by alcohol and, when evaporated to dryness and ignited, it should leave no appreciable residue.

## BARIUM PEROXIDE

$BaO_2 = 169·37$ (169)

White or greyish powder, insoluble in water; with dilute sulphuric acid it gives hydrogen peroxide.

Its value depends essentially on the proportion of $BaO_2$, which is determined in the following way: 0·2–0·3 gram is introduced, gradually and with shaking, into 300 c.c. of 10% sulphuric acid, the hydrogen peroxide thus formed being titrated with N/5-permanganate solution; 1 c.c. N/5-permanganate = 0·0169 gram $BaO_2$.

Commercial barium peroxide usually contains 80–85% of $BaO_2$, the remainder being barium oxide and a few other impurities; some of the better grades contain, however, *90–91% $BaO_2$*.

## BARYTA (Barium Hydroxide)

$Ba(OH)_2 + 8H_2O = 315{\cdot}37$

Colourless, more or less opaque, lamellar crystals, or white or yellowish fused masses; in the crude state it forms more or less grey crystalline masses. It dissolves in 20 parts of cold, or 2 parts of boiling water, but complete solution is difficult owing to the presence of insoluble carbonate. Its impurities may be carbonate, sulphate, sulphide and thiosulphate of barium, chlorides, heavy, earthy and alkali metals. Its examination includes:

**1. Carbonate, Sulphate.**—2–3 grams are dissolved in dilute hydrochloric acid, effervescence indicating carbonate in considerable amount; insoluble residue may be barium sulphate.

**2. Sulphide.**—5 grams are dissolved in excess of hydrochloric acid and the solution heated, evolution of hydrogen sulphide being tested for with lead acetate paper; or, a few drops of lead acetate solution are added to the aqueous solution and any black precipitate noted.

**3. Sulphite, Thiosulphate.**—5 grams are treated with 50 c.c. of water and about 0·5 gram of cadmium carbonate (to eliminate the sulphide), the liquid being heated for about 30 minutes on the steam-bath and filtered. To the filtrate are added a little starch paste and then dilute iodine solution; in absence of sulphite and thiosulphate, a blue coloration appears immediately.

**4. Chlorides.**—2–3 grams, dissolved in dilute nitric acid, should not be rendered turbid by silver nitrate.

**5. Heavy Metals.**—The hydrochloric acid solution is treated with hydrogen sulphide and then with ammonia and ammonium sulphide; traces of lead and copper and small proportions of iron are to be tested for.

**6. Alkaline Earths, Alkalies.**—5 grams are dissolved in dilute hydrochloric acid, the solution heated and the barium precipitated with sulphuric acid and filtered. The filtrate should remain clear on addition of alcohol and should leave no sensible residue on evaporation in a platinum dish.

**7. Quantitative Determination.**—35–40 grams of the baryta are dissolved in boiled water and the volume made up to 1 litre. The following determinations are made on aliquot parts of this solution removed by means of a burette with automatic filling device, in order to avoid the action of atmospheric carbon dioxide.

(*a*) *Barium hydroxide.* 25 c.c. of N/5-hydrochloric acid, plus about 200 c.c. of water and 10–12 drops of 0·5% methyl orange solution, are titrated with the baryta solution, the point of neutrality being taken as the change from orange yellow to a distinct yellow. 25 c.c. N/5-HCl = 0·7885 gram $Ba(OH)_2 + 8H_2O$.

(*b*) *Hydrogen sulphide and thiosulphuric acid.*

(1) 200 c.c. of the baryta solution are acidified with acetic acid in a half-litre bottle with a ground stopper, a little starch paste being then added and the liquid titrated with about N/10-iodine solution. The iodine solution is previously titrated with N/10-sodium thiosulphate solution.

(2) 200 c.c. of the baryta solution are treated in a 250 c.c. flask with a little cadmium carbonate suspended in water and heated for about 30 minutes on a steam-bath with frequent shaking. On cooling, the liquid is made up to 250 c.c. and filtered through a dry paper, 200 c.c. of the filtrate, acidified with acetic acid, being titrated with iodine in presence of starch paste.

The first titration gives the iodine consumed by the sulphides and thiosulphates and the second that consumed by the thiosulphates alone; it is easy, therefore, to deduce the thiosulphuric acid and hydrogen sulphide, which are calculated as barium salts.

(*c*) ***Other determinations.*** Commercial baryta does not usually contain lime and free alkali in appreciable quantity; otherwise the volumetric determination of the baryta gives inaccurate results.

The presence of other bases is readily detected indirectly, by determining the barium in 25 c.c. of the aqueous solution—prepared as above—gravimetrically as sulphate and calculating it as crystallised barium hydroxide. If this result is lower than that obtained volumetrically, the latter must be erroneous owing to the presence of other bases.

## BLEACHING POWDER
## (Chloride of Lime)

$CaOCl_2 = 127$

White, hygroscopic powder with an odour of chlorine, partially soluble in water and soluble in hydrochloric acid with evolution of chlorine. The commercial value depends on the content of available chlorine. That to be used for bleaching textiles should be tested for iron and manganese.

**Determination of the Available Chlorine** (Penot and Lunge's method).—10 grams are well pounded in a mortar with a little water, further quantities of water being gradually added with constant mixing. The whole of the liquid and solid matter is introduced into a litre measuring. flask and made up to the mark and mixed, 50 c.c. of the turbid liquid being immediately removed. Into this liquid standard sodium arsenite [1] is run slowly from a burette with gentle shaking until a drop of the solution no longer colours starch-iodide paper.[2] The end-point is easily fixed, since the coloration of the paper gradually weakens beforehand.

The number of c.c. of arsenite used, multiplied by 2, gives the number of litres of chlorine (at 0° and 760 mm.) per kilo of substance. This represents the *chlorometric degree, Gay-Lussac degree* or *French degree* of the chloride. To obtain the percentage of chlorine by weight (*English, German, American degree*), the chlorometric degree must be multiplied by 0·31698.

[1] 4·425 grams of arsenious acid (puriss.) and 13 grams of crystallised sodium carbonate (puriss.) are dissolved in hot water and the volume made up to 1 litre after cooling.

[2] 3 grams of pure potato starch are mixed with 250 c.c. of cold water and boiled with constant stirring; 2 grams of pure potassium iodide and 1 gram of crystallised sodium carbonate are added and the volume made up to 500 c.c. Strips of filter-paper, after immersion in this liquid, are allowed to dry and kept in well closed vessels.

The same method serves for determining the available chlorine in other bleaching chlorides such as *sodium hypochlorite* (*Eau de Labarraque*) and *potassium hypochlorite* (*Eau de Javelle*), etc.

Good commercial chloride of lime usually furnishes 123–127 chlorometric degrees, corresponding with 39–40% of available chlorine; lower qualities give as little as 95 degrees (30% of chlorine).

## BORAX AND NATURAL BORATES

The most common *sodium borate* is the *prismatic* form, $Na_2B_4O_7 + 10H_2O = 382{\cdot}26$, with 47·14% of water. There are also *Octahedral borax*, $Na_2B_4O_7 + 5H_2O = 292{\cdot}26$, with 30·83% of water, and *Burnt borax*, $Na_2B_4O_7 = 202{\cdot}1$, free from water. The first two form crystals, prismatic or octahedral, and the third a fine powder, and all dissolve in water with an alkaline reaction.

Natural borates are: *Boracite* (magnesium borate and magnesium chloride, $2Mg_3B_8O_{15} + MgCl_2$), *Borocalcite* or *Pandermite* (hydrated calcium borate, $Ca_2B_6O_{11} + 4H_2O$ or $CaB_4O_7 + 6H_2O$) and *Boronatrocalcite* (calcium borate and sodium hydroxide).

Borax may contain the same impurities as boric acid (*q.v.*). In borax and the natural borates the content of boric acid must be determined; this may be done either by difference after the water and the impurities have been determined or directly by a volumetric method.

**Determination of the Boric Acid.**—(*a*) IN BORAX: about 30 grams of the substance are dissolved in boiled water and the solution made up to 1 litre. 50 c.c. of the liquid, filtered if necessary, are titrated in presence of a few drops of methyl orange with N/2-acid, which combines with the $Na_2O$ and liberates all the boric acid. 50 c.c. of glycerine and 2–3 drops of phenolphthalein solution are then added and the solution titrated with N/2-alkali hydroxide (absolutely free from carbonates), as indicated under Boric Acid (5). 1 c.c. of N/2-acid = 0·0155 gram $Na_2O$ and 1 c.c. N/2-alkali = 0·0175 gram $B_2O_3$ = 0·0955 gram $Na_2B_4O_7 + 10H_2O$.

(*b*) IN NATURAL BORATES: 2 grams of the substance are heated, in a flask with a reflux condenser, with 50 c.c. of N-acid. When cool, the condenser is rinsed out and the excess of acid neutralised with N-alkali in presence of methyl orange. Glycerine and phenolphthalein are then added and the free boric acid titrated with N/2-alkali as in case (*a*).

*Crude* borax may contain marked quantities of impurities (sodium chloride and sulphate, calcium sulphate, insoluble matters and hygroscopic water); the *refined* product is generally pure or almost so. The boronatrocalcite of S. America contains 21–44% $B_2O_3$.

## BROMINE

Br = 79·92 (80)

A dark, brownish-red, heavy liquid emitting in the air irritating, dense red fumes; soluble in about 33 parts of water, D = 2·99 at 15°, b.pt. 63°. *It may be contaminated* with chlorine, iodine, sulphuric acid, and organic

compounds (bromoform, bromocarbonates). Its analysis includes the following tests:

**1. Fixed Residue.**—A few grams of bromine are allowed to volatilise in a porcelain dish; pure bromine leaves no weighable residue.

**2. Organic Substances.**—A few grams are dissolved in water and excess of ammonia added; in presence of organic bromine compounds, a turbid solution is obtained from which oily drops may separate.

**3. Sulphuric Acid.**—Part of the preceding ammoniacal solution is acidified with hydrochloric acid and tested with barium chloride.

**4. Iodine.**—Another part of the ammoniacal solution is evaporated to dryness and the residue redissolved in water and treated with a few drops of ferric chloride solution; in presence of iodine, the liquid is coloured yellow and gives a violet colour to carbon disulphide when shaken with this.

**5. Chlorine.**—Another part of the ammoniacal solution is evaporated to dryness, 0·1 gram of the residue being dissolved in 10 c.c. of water and 4 c.c. of ammonium carbonate solution (1 part of the carbonate, 1 part of ammonia of D 0·96 and 3 parts of water); 12 c.c. of N/10-silver nitrate are then added, and the liquid heated for a short time to 50–60° and filtered, the filtrate being acidified with nitric acid. With pure bromine, the liquid is scarcely milky, but if chlorine is present a precipitate of silver chloride is formed.

For a rapid determination, which is sufficiently exact, Kubierschki's method [1] may be used.

Commercial bromine is generally pure; that of the Stassfurt-Leopoldshall Mining Syndicate is guaranteed to contain less than 0·3% of chlorine.

## CALCIUM ACETATE

$$Ca(C_2H_3O_2)_2 = 158{\cdot}15$$

The pure salt is put on the market in colourless crystals extremely soluble in water, but is of limited application; the crude salt (*calcium pyrolignite*), in brownish-grey, hygroscopic lumps or coarse powder with a marked empyreumatic odour, is an important raw material for the manufacture of acetic acid and other acetates. This crude salt is always contaminated with tarry substances, and also contains small quantities of formate, propionate and other organic salts of calcium, calcium carbonate, alumina, ferric oxide, etc.; its value depends on its content of pure calcium acetate or acetic acid, so that importance attaches to the quantitative determination of the acid.

**Determination of the Acetic Acid.**—Use is made of a tubulated retort of 200 c.c. capacity placed on a sand-bath, the neck being turned up a little and connected with a condenser by means of an obtuse-angled tube. In this, 5 grams of the acetate, 50 c.c. of water and 50 c.c. of ordinary phosphoric acid (D = 1·20) free from nitric acid are heated and distilled almost to dryness, the liquid being collected in a 250 c.c. measuring-flask; after cooling, the retort is charged with another 50 c.c. of water and distillation almost to dryness repeated. At the end of the distillation, the

[1] *See Post, Chem.-techn. Analyse.*

volume is made up to the mark with distilled water and, after mixing, 50 or 100 c.c. are titrated with N-alkali in presence of phenolphthalein. 1 c.c. of N-alkali = 0·07907 gram of anhydrous calcium acetate = 0·06003 gram of acetic acid.

It is well to ascertain that the distillate does not contain appreciable quantities of hydrochloric acid derived from chlorides in the acetate (silver nitrate should give at most a faint opalescence). The small amounts of propionic and butyric acids, etc., are practically negligible.

* * *

Crude calcium acetate (pyrolignite) usually contains 70–80% of true anhydrous acetate and hence 53–60% of acetic acid. The pure calcium acetate used in dyeing is mostly prepared by the consumer himself by dissolving lime or calcium carbonate in acetic acid ; it should particularly be free from iron.

## CALCIUM CARBIDE

$CaC_2 = 64$

Fused masses with crystalline fracture, greyish-brown in colour and alterable in moist air. With water it decomposes, giving acetylene and calcium hydroxide. It may contain, as impurities, calcium sulphide and phosphide, ammonium sulphide, silica, ferrosilicon and silicon carbide, its value depending essentially on its yield of acetylene. The product being always non-homogeneous, special care attaches to sampling.

**1. Sampling.**—According to the number of casks (drums) in the parcel to be analysed, a sample of at least 2 kilos is taken from a cask (for lots up to 20 drums) or from 5% or 10% of the casks (for lots of more than 20 drums). Before being opened the cask is inverted twice to distribute the small pieces and dust as uniformly as possible throughout the coarse. The sample is placed immediately in glass vessels with ground stoppers or in metal vessels with soldered lids.[1]

**2. Various Impurities.**—As a rule the carbide itself is not investigated, it being sufficient to determine the yield of acetylene and to test the purity of the gas (*see* below). Where necessary, however, the carbide may be treated with a sugar solution in which the lime remains dissolved, whereas the impurities remain undissolved and may be recognised by the ordinary analytical methods. As a rule these impurities represent 3–6% of the carbide.

**3. Yield of Acetylene.**—This is determined by treating a known weight of the carbide with water (or, better, brine) and measuring the volume of gas evolved. Various forms of gasometer or apparatus may be used to collect and measure the gas.[2]

The determination may be made in one of two methods : *Total gasification*, which consists in decomposing with water (in one or more lots) the whole of the sample as it is taken, and *Partial gasification*, which consists

[1] See also *Acetylene*, by V. B. Lewes (New York, 1900), Post, *Chem.-techn. Analyse.*

[2] See works cited in preceding note, and also articles by Formenti in *La chimica industriale*, 1902, Vol. VI, p. 182 ; Recchi in *Gazz. chim. ital.*, 1903, I, p. 153 ; Magnanini and Vannini, *ibid.*, 1900, I, p. 401.

in powdering the sample rapidly and then decomposing two or more aliquot parts of the powder.

**4. Purity of the Acetylene.**—The acetylene may contain various impurities, such as hydrogen phosphide and sulphide, ammonia, hydrogen, nitrogen, oxygen and carbonic oxide. Of these the most important to detect and estimate is hydrogen phosphide. Lunge and Cedercreutz's method may be used for this purpose : 50 grams of the carbide are placed in a flask of about ½ litre capacity closed by a stopper with two holes, through one of which passes a tapped funnel and through the other a right-angled tube connected with a tube with 10 bulbs into which are poured 75 c.c. of 2–3% sodium hypochlorite solution. From the funnel water is dropped slowly on to the carbide, which is occasionally shaken. When the evolution of gas ceases, the flask is nearly filled with water and gentle suction applied to the bulb-tube, so that all the gas traverses the hypochlorite. The contents of the bulb-tube are then introduced into a beaker and the phosphoric acid (formed by the action of the hypochlorite on the hydrogen phosphide) precipitated with magnesia mixture (*see* Fertilisers). 1 gram of magnesium pyrophosphate = 0·81982 gram of calcium phosphide ($Ca_3P_2$) = 200·86 c.c. of hydrogen phosphide ($PH_3$).

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Commercial calcium carbide in lumps or pieces should not contain more than 5% of fine dust passing through a sieve of 1 mm. mesh, and the impurities should not exceed 3–6%. Good carbide usually gives about 300 litres (at 15° and 760 mm.) of acetylene per kilo, whilst the chemically pure product should give 348·8 litres. A commercial carbide should not give less than 270 litres per kilo, with an allowance of 2% on the analytical results. The impurities in the gas should not exceed 1%. Of these hydrogen sulphide or ammonia is found rarely and only in traces, but hydrogen phosphide occurs in relatively large proportions ; Lunge and Cedercreutz have found from 0·031 to 0·061% by volume, which would correspond with about 0·038–0·075 gram of calcium phosphide per kilo of carbide (with a yield of 300 litres of gas).

## CALCIUM CITRATE

$$Ca_3(C_6H_5O_7)_2 + 4H_2O = 570$$

Crude calcium citrate, prepared largely in Sicily, serves as raw material for the preparation of citric acid. It forms yellowish-grey clots or powder with a slight biscuity odour and dissolves slightly in cold water with an alkaline reaction and still less in hot water. It consists mostly of calcium citrate, mixed with calcium carbonate and oxide, with small proportions of other salts and organic compounds of calcium, ferric oxide, alumina, silica, etc. ; in some cases it contains magnesia and strontia.

The commercial value of calcium citrate depends on the quantity of crystallised citric acid corresponding with the pure calcium citrate contained in the product. The quantitative estimation of the citric acid hence occupies first place in the analysis ; then come determinations of the alkalinity, hygroscopic moisture and ash, and a partial qualitative analysis to detect any such adulteration as sulphate, oxalate, phosphate, tartrate of calcium, etc.

**Preparation of the Sample.**—Prior to the analysis, the sample must be thoroughly mixed by pounding in a glass mortar and passing it several times through a fine sieve. The sample is then stored in tight vessels.

**1. Alkalinity.**—About 5 grams are carefully boiled for some minutes in a 100 c.c. flask with 25–30 c.c. of N/2-hydrochloric acid; on cooling, the excess of acid is titrated with N/2-alkali in presence of phenolphthalein. The alkalinity is expressed as calcium carbonate, so that the number of c.c. of acid neutralised, multiplied by 0·025, gives the alkalinity referred to 100 grams of the citrate.

**2. Loss of Weight at 100°.**—2–3 grams are dried in a steam-oven for about 5 hours in a weighing bottle 5 cm. wide and 3 cm. high, weighed and again heated to constant weight. The loss of weight is referred to 100 grams of citrate, which, when pure, loses 4·73% of water of crystallisation.

**3. Hygroscopic Water.**—From the loss in weight at 100° and the percentage of citric acid or, better, calcium citrate (*see* 6, below) in the sample the hygroscopic moisture is calculated.

Example: A sample of citrate contains 62·40% of citric acid or 84·72% of pure calcium citrate, and loses in the steam-oven 5·08% of its weight. Since 100 grams of pure citrate lose 4·73 grams, the water of crystallisation lost by the calcium citrate in the sample will be given by

$$100 : 4{\cdot}73 :: 84{\cdot}72 : x$$
$$x = 4{\cdot}00.$$

The hygroscopic moisture is, therefore, 5·08–4·00 = 1·08%.

With commercial citrates this procedure gives only approximate results, since the other substances present may influence the loss of weight in one direction or the other.

**4. Ash.**—About 10 grams in a platinum dish are heated first gently over a gas flame and then at a red heat in a muffle for an hour.

**5. Impurities.**—(*a*) PHOSPHATES. The citrate is sometimes adulterated with calcium phosphate. Part of the ash is heated with nitric acid and the solution filtered and tested for phosphoric acid by means of ammonium molybdate.

(*b*) MAGNESIUM AND STRONTIUM. For these the ash is tested by the ordinary methods.

(*c*) OXALATES. About 8 grams are dissolved in hot, dilute hydrochloric acid, filtered and the filtrate made up to 200 c.c. (solution *a*).

50 c.c. of this solution are diluted with distilled water, rendered alkaline with caustic soda and then acidified with concentrated acetic acid: no turbidity should appear.

(*d*) SULPHATES. To 50 c.c. of solution *a* barium chloride in slight excess is added.

(*e*) TARTRATES. The remaining 100 c.c. of solution *a* are rendered alkaline with potassium carbonate and evaporated to dryness. The residue is taken up in a little boiling water and filtered, the filtrate being acidified distinctly with acetic acid and 10 vols. of 95% alcohol added. The crystalline precipitate obtained is filtered off, washed two or three times with alcohol and dried in a steam-oven. A very small quantity of resorcinol and a few drops of concentrated sulphuric acid are gently heated in a porcelain dish until white fumes are emitted and a few crystals of the above

precipitate added and gentle heat again applied. A distinct wine-red coloration indicates the presence of tartaric acid.

**6. Determination of the Citric Acid.**—10 grams of the citrate are boiled gently in a graduated 250 c.c. flask with 22 c.c. of hydrochloric acid of D 1·10 and about 50 c.c. of distilled water to expel the carbon dioxide completely. When cold, the liquid is made up to the mark, shaken and filtered through a dry paper. 50 c.c. of the filtrate (= 2 grams of the citrate) are neutralised exactly with approximately 2N-caustic soda free from carbonate, using phenolphthalein as indicator. After addition of 2 c.c. of roughly 40% calcium chloride solution, the liquid is made faintly acid with a few drops (4–6) of N/2-hydrochloric acid.

This liquid, in a beaker of resistant glass, is kept for half an hour immersed in a bath of boiling brine and then filtered hot through a rapid filter, on to which the calcium citrate precipitate is washed as completely as possible with hot water; the precipitate is washed with boiling water, not more than 150 c.c. being used altogether. The precipitate (I) is then dried in a steam-oven, while the filtrate is neutralised with a few drops of dilute ammonia (1 : 6) and concentrated to 30–40 c.c. in the beaker previously used for the precipitation. The liquid is then placed in a smaller beaker (50 c.c.), another drop of ammonia being added and the concentration continued to 15 c.c. The precipitate is then collected on a small filter and rapidly washed with small quantities of boiling water.

This precipitate (II) is dried and the filtrate, treated as before with a little dilute ammonia, concentrated by boiling to 10 c.c. The precipitate (III) is collected on a small filter, washed with very small amounts of boiling water and dried in the steam-oven.

The three dry precipitates are incinerated with the filter-papers in a platinum dish and the latter kept in a muffle at redness for 30 minutes. The ash is then treated with 50 c.c. of N/2-hydrochloric acid, which is added to the dish in small portions, and then transferred to a flask. The liquid is boiled carefully to dissolve the ash completely, then cooled and the excess of acid titrated with N/4-potassium hydroxide in presence of phenolphthalein. The quantity of citric acid is then calculated; 1 c.c. of N/4-alkali = 0·0175 gram of crystallised citric acid or 0·875% on the sample.

This method has been officially adopted in Italy for the analysis of crude citrate and concentrated lemon juice.

Where marked quantities of tartrate have been found, it is advisable not to concentrate the solutions much for collecting precipitates II and III—instead of 15 and 10 c.c. only to 20 and 15 c.c. respectively.

In case sulphates are present, the ash from the precipitates should be treated with 10 c.c. of 3% hydrogen peroxide solution, which is then slowly evaporated on a water-bath, the treatment with 50 c.c. of N/2-hydrochloric acid being afterwards carried out as described above.

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Crude calcium citrate contains 64–70% of crystallised citric acid (+ $1H_2O$) in combination with lime; usually the percentage varies between 64 and 66, but impure samples containing 59–63% are not rare.

The alkalinity of the crude citrate, deduced from the free lime and calculated as calcium carbonate, should not exceed 2%, otherwise the price is subject to reduction.

The ash of the crude citrate is usually grey owing to the presence of ferric oxide and contains alumina, silica and alkalies; magnesium and aluminium, when present, should be in very small proportions. These two metals come from impure lime used in the manufacture of the citrate and lower the yield of the latter appreciably. Further, sulphates, phosphates and oxalates should occur only in minimal proportions.

In the steam-oven, crude citrates lose 4–6% of their weight. The pure citrate loses 4·73% at 100°.

## CARBON BISULPHIDE

$CS_2 = 76$

A colourless or yellowish liquid, of ethereal odour if highly pure but usually of repulsive smell owing to the presence of traces of organic sulphur compounds. It is very readily inflammable, D = 1·272, b.pt. 46–47°, insoluble in water. The commonest impurity is sulphur, and it may contain also hydrogen sulphide, sulphurous and sulphuric acids. The principal tests are as follows.

**1. Sulphur.**—5 c.c., allowed to evaporate spontaneously in a tared glass dish, should leave no weighable residue; or about 2 c.c. is shaken with a drop of dry, clean mercury, and note made if this becomes covered with a brown, powdery layer.

**2. Hydrogen Sulphide.**—The liquid is shaken with a little lead carbonate, which blackens in presence of hydrogen sulphide.

**3. Sulphurous and Sulphuric Acids.**—The sulphide is shaken with water coloured with a drop of neutral litmus solution and any decolorisation or reddening of the water noted.

## CARBON TETRACHLORIDE

$CCl_4 = 153·84$

Colourless liquid of ethereal odour, D = 1·6, b.pt. 76–77°, insoluble in water, miscible in all proportions with alcohol or ether. It may be contaminated with chlorine, hydrochloric acid, aldehydes, various organic impurities and carbon bisulphide. The tests to be made are as follows:

**1. Volatility.**—25 c.c., evaporated on a steam-bath, should leave no appreciable residue.

**2. Chlorine and Hydrochloric Acid.**—*See* Chloroform.

**3. Aldehydes.**—10 c.c. are shaken with 10 c.c. of potassium hydroxide solution (1 : 3) and heated for 1 minute: the aqueous liquid should not colour.

**4. Organic Impurities.**—20 c.c. are shaken with 15 c.c. of pure conc. sulphuric acid, which should not colour within an hour.

**5. Carbon Bisulphide.**—10 c.c. are mixed with 10 c.c. of alcoholic potassium hydroxide (1 gram in 10 c.c. of absolute alcohol); after an hour, the liquid is faintly acidified with acetic acid and 1–2 drops of dilute copper sulphate solution added; no browning or yellow precipitate (*potassium xanthate*) should be produced within two hours.

## CHLORIDE OF LIME

*See* Bleaching Powder

## CHLOROFORM

$CHCl_3 = 119{\cdot}38$

Colourless heavy liquid of peculiar odour, D = 1·490–1·493, b.pt. 61–62°, very slightly soluble in water, miscible with alcohol. The impurities to be looked for are especially chlorine, hydrochloric acid, chloro-compounds (of ethylidene and amyl) and aldehydes, the tests being carried out as follows :

**1. Volatility.**—20–30 c.c., evaporated spontaneously or at a gentle heat, should leave no appreciable residue of unpleasant, irritating odour (*phosgene, amyl* or *valeric compounds*).

**2. Reaction, Hydrochloric Acid.**—To 5 c.c. are added 1 drop of a saturated solution of Congo red in absolute alcohol : if the chloroform has undergone change, a blue coloration appears.

5 c.c. are shaken with 2·5 c.c. of water, which should not become acid or give a turbidity with silver nitrate (*hydrochloric acid*).

**3. Other Tests.**—5 c.c., shaken with potassium iodide solution or with iodide-starch paste, should give no red or blue coloration (*chlorine*).

20 c.c., shaken with 12 c.c. of pure conc. sulphuric acid, should give no brownish-yellow coloration, even after 24 hours (*chlorinated ethylidene* or *amyl compounds*).

A fragment of caustic potash, added to 5 c.c. of the sample, should remain white and the liquid should not turn yellow in 12 hours.

Pure chloroform for medical purposes should answer all the above tests. It is permissible to add 0·5–1% of alcohol as a preservative.

## COPPER SULPHATE

$CuSO_4 + 5H_2O = 249{\cdot}57$

Blue crystals which effloresce somewhat in the air, soluble in 3·5 parts of cold water. It is sold fairly pure, only containing, as a rule, small quantities of ferrous sulphate and rarely zinc, magnesium and calcium sulphates or free sulphuric acid. Its value depends on the proportion of pure crystallised copper sulphate and its analysis includes mainly determinations of the copper and water (3 and 4). In some cases determinations of the iron and free sulphuric acid may be required.

**1. Iron.**—4 grams are dissolved in 20 c.c. of water, an excess of ammonia added, the liquid filtered and the filter washed until it is no longer blue ; in presence of iron, a brownish deposit or spot remains on the filter.

**2. Zinc, Magnesium, Calcium and other Metals.**—2 grams are dissolved in 40 c.c. of water, the solution being acidified with hydrochloric acid and the copper precipitated with hydrogen sulphide ; the filtered liquid, evaporated and ignited, should leave no appreciable residue. If

this is not the case, the extraneous substances are examined in the ordinary way.

**3. Determination of the Copper.**—This may be carried out electrolytically or volumetrically.

(*a*) ELECTROLYTIC DETERMINATION. 4–5 grams of the sample, as homogeneous as possible, are dissolved in about 200 c.c. of water with gentle heating; 5–6 c.c. of conc. nitric acid and 20 c.c. of dilute sulphuric acid (10% by volume) are added and the solution electrolysed (*see* article on Copper in chapter on Metals). The conditions of working are as follows: Winkler electrodes; $ND_{100} = 0{\cdot}3–0{\cdot}4$ ampere; voltage, 2–2·2 volts; temperature, ordinary; duration, 16–18 hours.

The weight of copper found, multiplied by 3·9283, gives the sulphate of copper, $CuSO_4 + 5H_2O$.

(*b*) VOLUMETRIC DETERMINATION (Zecchini's method [1]). For this method the following reagents are required:

(*a*) Solution containing 19·878 grams of crystallised sodium thiosulphate per litre and another, 8 grams of ammonium thiocyanate per litre.

(*b*) Iodine solution containing 5·089 grams of iodine and 20–25 grams of potassium iodide per litre.

(*c*) Pure copper sulphate solution containing 20 grams of the crystals per litre.

Solutions (*a*) and (*c*) are of corresponding strength and 2 vols. of (*b*) correspond with 1 vol. of (*a*).

In a porcelain dish are placed 60 c.c. of solution (*a*) and a little starch paste [2]; solution (*b*) is then run in from a burette until a persistent blue coloration appears. To another 60 c.c. of (*a*) are added, with stirring, 50 c.c. of solution (*c*) (= 1 gram of $CuSO_4$, $5H_2O$) and 10 c.c. of starch paste, this being titrated with iodine (*b*) as before.

The difference (*n*) between the volumes of (*b*) used in the two cases corresponds with 1 gram of $CuSO_4$, $5H_2O$, and with pure materials under the above conditions, this difference is very nearly 100 c.c., as it should be.

The operation is then repeated with a solution (20 grams per litre) of the sulphate to be tested, 50 c.c. being taken and the volume of the iodine solution necessary measured. If $n^1$ is the difference in the volume of (*b*) used in this case, the percentage of pure crystallised copper sulphate is $(100 \times n^1)/n$.

**4. Water.**—5 grams of the powdered sulphate are weighed in a platinum crucible, which is supported on a porcelain triangle inside a larger iron crucible; the latter is heated for 15 minutes with a large Teclu flame, the platinum crucible being then cooled in a desiccator and weighed.

**5. Iron.**—5–10 grams, dissolved in 100–150 c.c. of water, are heated for 15 minutes on a steam-bath with 5–10 c.c. of nitric acid, the iron being then precipitated with a slight excess of ammonia and weighed as $Fe_2O_3$: $Fe_2O_3 \times 3{\cdot}475 = FeSO_4 + 7H_2O$.

**6. Free Sulphuric Acid.**—10 grams are dissolved to 500 c.c., the

[1] *Stazioni agrarie italiane*, Vol. XXXII, p. 120.

[2] 3 grams of starch are mixed to a paste with a little water and poured into 200 c.c. of boiling water, the solution being boiled for a minute and allowed to cool.

acidity being determined on an aliquot part by N/10-alkali, Congo-red paper being used as indicator. 1 c.c. N/10-alkali = 0·0049 gram $H_2SO_4$.

Commercial copper sulphate usually contains 98–99·5% of $CuSO_4 + 5H_2O$.

## ETHER

$C_4H_{10}O = 74$

Colourless, light, highly volatile, neutral liquid, of peculiar odour, D = 0·720–0·722, b.pt. 35°, slightly soluble in water (10–12%) and miscible with alcohol. Commercial ether almost always contains more or less marked quantities of water, alcohol and free acids ; old aqueous ether may contain hydrogen peroxide or other peroxidised compounds, which may cause explosions when the ether evaporates. The tests to be made, besides determinations of the density and boiling point, are as follows :

**1. Water.**—When shaken with aqueous ether, anhydrous copper sulphate is coloured blue, whereas if the ether is anhydrous it remains white. A piece of freshly cut sodium, immersed in perfectly anhydrous ether, retains its lustre for some hours ; if the ether is wet, the sodium becomes covered immediately with an opaque layer, while copious evolution of hydrogen occurs.

**2. Alcohol.**—10 c.c., shaken with as much water (in a closed cylinder), should not diminish in volume by more than one-tenth ; the water separated should not give the iodoform reaction with iodine and caustic soda.

**3. Acidity.**—To 20 c.c. are added 10 c.c. of water and a few drops of phenolphthalein and, after shaking, the volume of standard alkali necessary to produce a red coloration determined. With a good sample this should not exceed 0·1–0·2 c.c. of N/100-alkali.

**4. Hydrogen or other Peroxide.**—10 c.c. are shaken in a closed cylinder with 1 c.c. of 1 : 10 potassium iodide solution : with pure ether, no coloration should occur, even after an hour's stand in the dark.

**5. Aldehydes, Vinyl Products.**—5 c.c. should give no coloration within 5 minutes with 1 c.c. of water and 5 drops of Nessler reagent.

**6. Sulphur Compounds.**—10 c.c. are shaken with a few drops of well cleaned mercury, which becomes brown or black in presence of sulphur compounds.

## FERRIC CHLORIDE

$FeCl_3 + 6H_2O = 270{\cdot}22$

Orange-yellow, deliquescent, crystalline masses, which may contain oxychloride (insoluble), free chlorine and hydrochloric acid, ferrous chloride, arsenic, nitrates and extraneous metals.

**1. Solubility.**—1 part of the salt and 1 part of water should, in absence of oxychloride, give a clear solution which remains clear after addition of 5 vols. of alcohol.

**2. Free Chlorine and Hydrochloric Acid.**—In the vessel containing the salt are suspended a moistened starch-iodide paper and a glass rod wet

with ammonia : in presence of chlorine, the paper turns blue and in presence of hydrochloric acid white fumes form round the rod.

**3. Ferrous Chloride.**—The 1 : 100 solution is tested with a few drops of freshly prepared dilute potassium ferricyanide solution : in presence of ferrous salts a blue coloration is formed.

**4. Arsenic.**—To 1 c.c. of the 1 : 1 solution, 5 c.c. of Bettendorf's reagent are added : no brown coloration should be formed within an hour.

**5. Nitrates and Extraneous Metals.**—1 gram, dissolved in 20 c.c. of water, is treated with excess of ammonia and filtered. 2 c.c. of the filtrate are boiled until the ammonia is completely expelled and is then mixed with conc. sulphuric acid, ferrous sulphate solution being poured carefully on to the surface of the liquid : any brown ring at the zone of contact of the two layers is observed (*nitric acid*).

The remainder of the filtrate is evaporated to dryness and calcined to ascertain if appreciable residue remains (*extraneous metals*).

## FERROUS ACETATE

Industrial use is made of crude ferrous acetate (*pyrolignite of iron*) solution, which is a greenish-black liquid of marked empyreumatic odour. This solution is usually of 12–15° Baumé, but stronger ones of 20–30° Baumé are also prepared, these containing more tarry matters which are precipitated on dilution.

**1. Grade.**—Determined with an ordinary Baumé hydrometer.

**2. Behaviour on Dilution.**—1 vol. is diluted with 250 vols. of water and the colour of the liquid and any precipitation of tarry substances noted.

**3. Ferric Salts.**—The sample is diluted 1 : 10, acidified with hydrochloric acid and tested with potassium ferrocyanide.

**4. Sulphates, Chlorides.**—The 1 : 10 solution of the sample is acidified with nitric acid and tested with barium chloride and with silver nitrate. An appreciable proportion of sulphate is determined as barium sulphate, while hydrochloric acid may be estimated as silver salt.

**5. Determination of the Acetic Acid.**—This is done as in calcium acetate (*q.v.*).

**6. Determination of the Iron.**—1–2 grams are evaporated to dryness and the residue cautiously ignited and dissolved in hydrochloric acid, the iron being determined in the solution by precipitation with ammonia.

Pyrolignite of iron solution or *mordant for black* (not to be confused with the basic sulphate), when diluted with water (test 2), should give a fine blue coloration, which slowly changes to greenish and becomes opaque; it should not contain any large proportions of ferric salts or sulphates.

## FERROUS SULPHATE

$$FeSO_4 + 7H_2O = 278$$

Forms large or small, pale green crystals or crystalline powder; in the air it effloresces somewhat, and it dissolves in 1·5 parts of water and is insoluble in alcohol. It often exhibits yellowish spots of ferric oxide or

sulphate. As impurities it may contain especially copper, zinc, manganese, magnesium, arsenic, ferric salts and free sulphuric acid.

**1. Copper, Zinc.**—3 grams are dissolved in water, boiled with nitric acid, and precipitated with excess of ammonia ; after filtration, the filtrate is tested for copper and zinc by the ordinary methods.

**2. Ferric Salts.**—The sample is dissolved in recently boiled water, acidified with a little hydrochloric acid and tested with ammonium thiocyanate.

**3. Free Sulphuric Acid.**—The aqueous solution, prepared with boiled water, should not redden blue litmus paper.

**4. Other Impurities.**—3 grams are dissolved in water and oxidised by boiling with nitric acid ; after precipitation with ammonia and filtration, the lime, magnesia, arsenic and any other impurities are sought in the filtrate.

## FORMALDEHYDE

$CH_2O = 30$

This is sold in aqueous solution under the name *Formol* or *Formalin* and is a colourless liquid with a peculiar, irritating odour, D = about 1·08 ; it contains 35–40 grams of formaldehyde per 100 c.c. The commercial product may be contaminated with formic and acetic acids, methyl alcohol, acetone, chlorides, sulphates, copper and calcium ; its value depends essentially on the content of formaldehyde.

**1. Acidity.**—Tested with litmus paper ; an acidity corresponding with a drop of N-alkali per 1 c.c. of the sample is allowable.

**2. Sulphuric Acid, Hydrochloric Acid, Metals.**—These are detected in the 1 : 5 solution in the usual way.

**3. Methyl Alcohol.**—50 c.c. are treated with 100 c.c. of 10% ammonia, with which the formaldehyde combines, forming hexamethylenetetramine ; after a rest of 6 hours in a closed vessel, the greater part of the liquid is distilled off. The distillate is acidified with a slight excess of dilute sulphuric acid and redistilled, the temperatures at which the first fractions distil being observed : in presence of methyl alcohol, these will come over at about 66° and may be tested for methyl alcohol (*see* Spirits : Detection of Denaturants).

By collecting 50 c.c. of distillate (after acidification) and determining its specific gravity, the quantity of methyl alcohol present may be found approximately from the table on p. 40.

**4. Acetone.**—A few c.c. are treated with sodium hydroxide and iodine solution : in presence of acetone, iodoform is formed immediately in the cold.

**5. Determination of the Formaldehyde** (Iodometric method of Fresenius and Grunhut).—25 c.c. are diluted with water to 500 c.c. and 5 c.c. of the solution (= 0·25 c.c. of substance) introduced into a bottle of about 200 c.c. capacity fitted with a ground stopper ; 30 c.c. of N-sodium hydroxide are then added rapidly from a graduated cylinder and, from a burette and with shaking, 50 c.c. of N/5-iodine solution (the liquid should

remain yellow). The vessel is then closed and shaken vigorously for half a minute, after which 40 c.c. of N-sulphuric acid are added from a graduated cylinder. The vessel is again closed and left for a few minutes, the excess of iodine being then titrated with N/10-sodium thiosulphate solution. 2 c.c. of N/10-thiosulphate = 1 c.c. N/5-iodine = 0·003 gram $CH_2O$. The number of c.c. of N/5-iodine consumed × 1·2 = grams of $CH_2O$ per 100 c.c.

This method is not applicable in presence of acetone, at any rate in appreciable quantity; as a rule, however, the proportion of acetone is small.

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Commercial formaldehyde should contain not less than 35 grams of $CH_2O$ per 100 c.c. Methyl alcohol is often added in the proportion of 10–25% by volume with the view of preventing polymerisation of the aldehyde, especially in concentrated solutions (about 40%). Occasionally the methyl alcohol is replaced by other products, such as ordinary alcohol, acetone, calcium chloride, etc.

## HYDROGEN PEROXIDE

$H_2O_2 = 34$

Colourless, clear, odourless liquid. With permanganate it effervesces briskly, liberating oxygen and decolorising the permanganate. When acidified with a little dilute sulphuric acid, treated with a few drops of potassium chromate and shaken with ether, the latter is coloured blue.

Commercial hydrogen peroxide almost always contains various impurities, especially sulphuric, hydrochloric, nitric, phosphoric, silicic, hydrofluoric and hydrofluosilicic acids (free and combined), aluminium, iron, calcium, barium, magnesium, alkalies and ammonia. It may also contain traces of arsenic, and, as an adulterant, oxalic acid. The following determinations are made.

**1. Sulphuric, Hydrochloric, Nitric and Phosphoric Acids.**—These are detected by the usual reagents.

**2. Silica.**—After evaporation of the sample, the residue is tested for silica in the ordinary way.

**3. Hydrofluosilicic Acid.**—The liquid is evaporated to small volume and tested with potassium chloride (white, gelatinous precipitate).

**4. Oxalic Acid.**—The liquid is treated with excess of ammonia, rendered acid with acetic acid and tested with calcium chloride.

**5. Metals, Alkaline Earths, Alkalies.**—These are detected by the ordinary reagents (ammonia, ammonium sulphide, ammonium oxalate, sodium phosphate, etc.), the liquid itself or its evaporated residue being used. Iron may be detected with ammonium thiocyanate.

**6. Fixed Residue.**—50 or 100 c.c. are evaporated in a tared dish on a steam-bath, the residue being dried at 110° and weighed.

**7. Acidity.**—10 c.c. are titrated with N/10-alkali in presence of phenolphthalein.

**8. Determination of the Active Oxygen.**—By active oxygen is meant the volume of oxygen yielded by 1 vol. of the peroxide. 25 c.c. of the liquid are diluted to 250 c.c. and 10 c.c. of this solution (= 1 c.c. of the peroxide) are diluted with 100 c.c. of water, acidified with 4 c.c. of

sulphuric acid and titrated in the cold with permanganate. With a solution of 5·65 grams of pure potassium permanganate per litre, each c.c. corresponds with 1 vol. of oxygen; using N/10-permanganate, 1 c.c. = 0·5596 vol. of oxygen and 1 vol. of oxygen = 0·3 gram $H_2O_2$.

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Commercial hydrogen peroxide usually contains 3–3·6% of $H_2O_2$, and thus yields 10–12 vols. of oxygen. Nowadays solutions of 30% or 50% or even higher concentrations are prepared, these giving 100, 160 or more vols. of oxygen. That intended for bleaching textiles should contain only traces of iron, alumina and barium[1]; an acidity corresponding with 1·5 gram of sulphuric acid per litre (3 c.c. of N/10-alkali per c.c.) is allowable.[2] Pure hydrogen peroxide for pharmaceutical purposes should be neutral or neutralisable by 2 or 3 drops of baryta and on evaporation should leave not more than 0·5 gram of fixed residue per litre; it should yield not less than 12 vols. of oxygen (Italian Pharmacopœia).

## HYDROSULPHITES

These are products used in dyeing and for decolorising sugar syrups, etc., and have various compositions and names, such as *Hydrosulphite, Rongalite, Hyraldite, Decroline* and *Blankite*. The active principle of these products is *sodium hydrosulphite*, $Na_2S_2O_4$, or *sodium hydrosulphite-formaldehyde* or *sulphoxylate*, $NaHSO_2$, $CH_2O + 2H_2O$, or the corresponding zinc salts. The action is regulated, according to circumstances, by addition of zinc oxide, lithopone, small quantities of catalytic substances (induline scarlet, patent blue, etc.). As impurities it may contain especially excess of water, bisulphite, sulphite and sulphate. The value depends on the content in active principle (hydrosulphite or sulphoxylate), which is determined as follows:

**Quantitative Determination.**—This is based on the reducing power of the hydrosulphites on indigo: 1 part of sodium hydrosulphite corresponds with 1·505 of pure indigo and 1 part of sodium sulphoxylate with 1·705 of indigo. The procedure is as follows:

(*a*) With Sodium Hydrosulphite. 1·505 gram of purest indigo and 9 grams of sulphuric acid (monohydrate) are heated for 6 hours at 40–50° with occasional shaking; after cooling, the mass is poured into water, the solution filtered, the filter thoroughly washed, and the filtrate made up to 1 litre.

Next 5 grams of the sample of hydrosulphite are dissolved in 10 c.c. of sodium hydroxide solution (38–40° Baumé), the volume being then made up to 500 c.c. with recently boiled water and the air in the neck of the flask replaced by illuminating gas. The solution is then drawn (not poured) into a burette.

100 c.c. of the indigo solution are introduced into a conical flask with a three-holed stopper traversed by the end of the burette containing the hydrosulphite solution, by a gas entry tube reaching almost to the surface of the liquid and by an exit tube. A current of illuminating

[1] Sisley, "Sur l'anal. de l'eau oxyg." in *Rev. gén. des mat. colorantes*, 1901, p. 209, and 1904, p. 164.

[2] Sisley, *loc. cit.*

gas is passed through the flask and the hydrosulphite solution run in, gradually and with shaking, until the blue colour of the indigo is replaced by a greenish-yellow colour. Dividing 1000 by the number of c.c. of hydrosulphite solution used, the percentage of $Na_2S_2O_4$ in the substance tested is obtained.

(*b*) WITH SODIUM SULPHOXYLATE (hydrosulphite-formaldehyde). The indigo solution is prepared as before, but with 1·705 grams of indigo. To 100 c.c. of this solution are added 10 c.c. of glacial acetic acid and the liquid heated for 5 minutes, illuminating gas being passed and the solution titrated with a solution of the sulphoxylate (10 grams per litre) as before. The percentage of $NaHSO_2$, $CH_2O + 2H_2O$ is obtained by dividing 1000 by the number of c.c. used.

With *zinc sulphoxylate*, 14 grams are dissolved in cold water together with 90 grams of ammonium chloride and 60 c.c. of 25% ammonia, the liquid being filtered and made up to a litre. This solution is used for the titration of 100 c.c. of the indigo solution (1·705 gram per litre), to which are added 10 c.c. of acetic acid, as above. If $n$ is the number of c.c. of the sulphoxylate solution used, the percentage of zinc sulphoxylate ($ZnHSO_2$, $CH_2O)_2O$ is given by $10930/14 \times n$.

## IODINE

$I = 126{\cdot}92$ (127)

Crude iodine forms small crystals or brown crystalline masses, while the resublimed product is in dark grey rhomboidal plates with metallic lustre; when heated it yields violet vapour. It dissolves in about 10 parts of alcohol and is soluble in carbon disulphide giving a violet solution and also in potassium iodide solution. The most common impurities are moisture, chlorine, bromine, cyanogen, small proportions of fixed substances, and graphite. The tests to be made are:

**1. Moisture.**—When shaken in a dry glass vessel, moist iodine becomes attached here and there to the walls.

To estimate the moisture, about 0·5 gram of the iodine is placed in a tube 1 cm. wide and 6 cm. long, 2–3 grams of powdered silver being then added and the whole weighed and gently heated until all the water is expelled (the upper layer of silver should remain unchanged), cooled and reweighed.

**2. Fixed Substances.**—1 gram is heated slowly in a porcelain dish until all the iodine is volatilised, the residue being weighed and examined (mineral substances, graphite).

**3. Cyanogen, Chlorine, Bromine.**—About 1 gram of the well powdered iodine is triturated with about 40 c.c. of water, the liquid being decanted off and divided into two portions:

(*a*) To one portion is added sufficient dilute sodium thiosulphate to decolorise it, then a crystal of ferrous sulphate, two drops of ferric chloride and a little soda; after heating, the liquid is acidified with hydrochloric

1. In presence of *cyanogen*, a coloration or precipitate of prussian blue ears.

(*b*) The other is rendered alkaline with ammonia, treated with excess of silver nitrate solution, shaken and filtered. The filtrate is then acidified with nitric acid, a precipitate being formed in presence of *chlorine* or *bromine* but only an opalescence, and that not immediate, when the iodine is pure.

**4. Quantitative Determination of the Iodine.**—In absence of appreciable proportions of chlorine or bromine, it is sufficient to dissolve a given weight (0·1–0·2 gram) of the iodine in potassium iodide solution (1 : 10) and to titrate with thiosulphate solution in presence of starch paste (1 c.c. of N/10-thiosulphate = 0·0127 gram of iodine).

In presence of chlorine and bromine, the iodine is dissolved in sodium hydroxide solution, sodium bisulphite solution and ferric chloride being added and the solution acidified with hydrochloric acid ; the liquid is then distilled in a suitable apparatus until all the iodine passes over. The iodine is collected in potassium iodide solution and titrated with thiosulphate.[1]

Crude commercial iodine may contain as much as 22% of moisture, and usually contains 74–94% of iodine. Resublimed iodine should contain 99–100%.

## LEAD ACETATE

$$Pb(C_2H_3O_2)_2 + 3H_2O = 379$$

The pure salt is in transparent, colourless crystals, which in dry air effloresce, losing water and acetic acid and absorbing carbon dioxide. The crude salt (*pyrolignite of lead*) forms yellowish fused masses of empyreumatic odour.

The pure acetate should answer to the tests 1–4 ; in the crude acetate the content of acetic acid is determined as in 5.

**1. Solubility.**—1 part in 5 parts of distilled water should give a clear, colourless solution.

**2. Chlorides, Sulphates.**—The 1 : 20 solution should not become turbid with either silver nitrate or barium chloride, even on standing.

**3. Copper.**—The 1 : 10 solution, treated with excess of ammonia and filtered, should give a colourless liquid.

**4. Iron, Alkaline Earth and Alkali Metals.**—The 1 : 20 solution treated with dilute sulphuric acid (or acidified with dilute hydrochloric acid and treated with hydrogen sulphide) until the lead is completely precipitated, should give a filtrate which leaves no appreciable residue on evaporation and ignition.

**5. Determination of the Acetic Acid.**—This is carried out as in calcium acetate (*q.v.*). 1 c.c. N-alkali = 0·379 gram of $Pb(C_2H_3O_2)_2 + 3H_2O$.

## MAGNESIA (Magnesium Oxide)

$$MgO = 40{\cdot}36 \ (40)$$

Pure magnesium oxide (*Magnesia calcinata*) is a light, white, amorphous powder which may contain, as impurities, magnesium carbonate and small

[1] Topf's method, *Zeitschr. f. analyt. Chem.*, 1887, p. 288.

proportions of extraneous salts (of calcium, alkalies, heavy metals). *Crude magnesia* (*calcined magnesite*), for technical uses, is in lumps or powder of colour varying from reddish-white to brownish-grey and may contain more or less considerable proportions of carbonates, ferric oxide, alumina, lime, silica and silicates.

Analysis of pure magnesia comprises essentially tests for the commoner impurities (1–4); the analysis of calcined magnesite necessitates various quantitative determinations, especially of the magnesium oxide, lime, iron, carbonates and silica (5–7).

**1. Carbonates, Insoluble Substances.**—1 gram, suspended in 10 c.c. of water and treated with 10 c.c. of dilute hydrochloric acid (1 : 1) should give, in the hot, a clear colourless solution without evolution of gas.

**2. Chlorides, Sulphates.**—The nitric acid (1 : 10) solution should give no turbidity with silver nitrate or barium chloride.

**3. Phosphates (and Arsenic).**—About 2 grams, dissolved in the least possible quantity of hydrochloric acid and treated with 40 c.c. of 10% ammonium chloride solution and 10 c.c. of ammonia (D = 0·910) should give no turbidity, even after 12 hours.

**4. Heavy Metals, Lime.**—1 gram, dissolved in dilute hydrochloric acid, should not be coloured blue by potassium ferrocyanide (*iron*) and should not be rendered turbid by hydrogen sulphide, even when alkaline with ammonia (*copper, lead, iron, zinc*); treated with a large excess of ammonium chloride and then with ammonia and ammonium oxalate, it should not become turbid even after 12 hours (*lime*).

**5. Determination of the Carbonates.**—Use is made of one of the methods indicated for the determination of carbon dioxide in limestones and clays (*see* Cement Materials).

**6. Determination of the Silica, Iron, Alumina and Lime.**—1–3 grams of the magnesia, according to its purity, are dissolved in conc. hydrochloric acid (better, in aqua regia) in the hot, the solution being evaporated to dryness and the residue heated at 110°, taken up in hydrochloric acid and filtered. The insoluble part remaining on the filter, after washing, igniting and weighing, gives the silica.

To the filtrate are added excess of ammonium chloride and slight excess of ammonia to precipitate the iron and aluminium, which are weighed as oxides in the usual way. In the filtrate from this precipitate the lime is precipitated with ammonium oxalate, which is redissolved in dilute hydrochloric acid and again precipitated with ammonium chloride, ammonia and ammonium oxalate; in this way the precipitate is freed from magnesia.

**7. Determination of the Magnesia.**—With calcined magnesite the total magnesia or that existing as oxide is required.

(*a*) TOTAL MAGNESIA (Meyerhofer's method). 5 grams of the finely powdered sample are evaporated to dryness with aqua regia on a steam-bath, the residue heated in an oven at 180–200° for 30 minutes and redissolved in a little hot hydrochloric acid, and the solution filtered and the filtrate made up to 1 litre.

Of this solution, 20 c.c. (= 1 gram of substance) are treated in a beaker successively with 5 c.c. of concentrated sulphuric acid, 100 c.c. of ammoniacal

citric acid solution (100 grams of citric acid and 333 c.c. of ammonia of D = 0·910 to 1 litre), 20 c.c. of 10% sodium phosphate and 15 c.c. of conc. ammonia solution (in this way the magnesia alone is precipitated as magnesium ammonium phosphate, the other bases remaining in solution). The liquid is well stirred for 5 minutes, left to stand for 2 hours and filtered (best through a Gooch crucible), the precipitate being washed, calcined and weighed as pyrophosphate; this weight, multiplied by 360, gives the percentage of MgO.

(*b*) MAGNESIUM AS OXIDE (Fortini's method).[1] This method requires a small calorimeter with a chamber unattackable by hydrochloric acid and an accurate thermometer; Tortelli's thermo-oleometer, described under "Fatty Substances" (General Methods, 21), serves excellently for this purpose.

In the chamber of the thermo-oleometer are placed 25 c.c. of hydrochloric acid (equal volumes of acid D = 1·19 and water), and after a few moments the temperature shown by the thermometer stirrer noted. An exactly weighed amount of the magnesia (0·5–1·0 gram) is then added and well mixed in until the temperature no longer rises. The total rise of temperature is proportional to the heat of the reaction, when a given calorimeter and a given quantity of acid are used. With Tortelli's thermo-oleometer and the above quantity of hydrochloric acid, 1 gram of MgO gives a rise of 37°.

The carbonates and other impurities of calcined magnesites give no appreciable rise of temperature on reaction with hydrochloric acid, but calcium oxide behaves exactly like magnesium oxide.

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Pure magnesia for pharmaceutical purposes or for chemical laboratories should correspond with tests 1–4. Calcined magnesite for making magnesia cements, dielectric or insulating materials, artificial stone, etc., should contain little carbonate (losing not more than 5% on calcination), not more than 4% of calcium oxide and 85–90% of magnesium oxide. That for metallurgical use (refractory materials) does not contain carbonates and may contain marked quantities of ferric oxide (up to 10%), as well as manganese oxide, lime, alumina and silica.

## MAGNESIUM CHLORIDE

$$MgCl_2 + 6H_2O = 203{\cdot}34$$

Colourless, deliquescent crystals, soluble in water or alcohol. It may contain sulphates and sodium salts more especially, and sometimes phosphates, heavy metals, lime and ammonia, these being tested for thus:

**1. Solubility.**—3 grams should give a clear solution with 15 c.c. of absolute alcohol if the salt is pure; any insoluble residue is tested for *sodium salts.*

**2. Sulphates.**—The 1 : 10 solution, acidified with hydrochloric acid, is tested with barium chloride.

**3. Phosphates.**—2 grams, dissolved in 40 c.c. of 10% ammonium

[1] *Ann. Lab. Chim. Gabelle*, Vol. VI, p. 509.

chloride solution, are treated with 6 c.c. of ammonia and any turbidity formed within 12 hours noted.

**4. Heavy Metals, Lime.**—The 1 : 20 solution is treated with hydrogen sulphide and any turbidity noted, either before or after addition of ammonia (*heavy metals*).

The same solution is treated wtih ammonium chloride in excess and then with ammonium oxalate (*lime*).

**5. Ammonia.**—*See* Stannic Chloride.

## MAGNESIUM SULPHATE

$$MgSO_4 + 7H_2O = 246{\cdot}32$$

Colourless crystals, readily soluble in 1·5 parts of water. It may be contaminated with chlorides, phosphates, arsenic, copper, iron, zinc, aluminium, lime and alkalies.

**1. Solubility, Chlorides.**—The aqueous solution should be clear and neutral and should not become milky with silver nitrate.

**2. Phosphates.**—5 grams, dissolved in 35 c.c. of water and treated with ammonium chloride and excess of ammonia, should give a limpid solution even after standing for hours.

**3. Arsenic.**—1 gram, treated with 5 c.c. of Bettendorf's reagent, should not colour within an hour.

**4. Metals, Earths.**—The 1 : 10 solution should not change with hydrogen sulphide, or ammonia, or ammonium sulphide, or ammonium oxalate, or potassium ferrocyanide.

**5. Alkalies.**—1 gram, dissolved in 30 c.c. of water, is boiled with 3 grams of barium carbonate and filtered : the filtrate should not react alkaline and should leave no appreciable residue on evaporation.

## MANGANESE DIOXIDE

$$MnO_2 = 86{\cdot}93 \ (87)$$

The product of this composition of the greatest practical importance is the natural *Pyrolusite*, which forms compact masses or small irregular pieces or more or less coarse powder. The mass has a radiating crystalline structure, a greyish-brown colour and an almost metallic lustre ; the powder is black.

Pyrolusite often occurs mixed with other oxides of manganese, such as *Braunite*, manganic oxide ; *Hausmannite*, mixed manganous-manganic oxide ; *Manganite*, hydrated manganic oxide ; *Psilomelan*, manganous oxide and manganese dioxide.

These minerals may contain also variable quantities of ferric oxide, alumina, baryta, magnesia and silica (gangue), and small amounts of lead or copper oxide, lime, alkalies, sulphates, phosphates and chlorides.

The value of the pyrolusite and of the other minerals depends on the

content of $MnO_2$, determination of which is the principal aim of the analysis; the latter may, however, be extended to the determination of moisture, total manganese, carbon dioxide and any other extraneous matters.

**1. Moisture.**—1–2 grams of the finely powdered substance are dried at 100° for 6 hours.

**2. Determination of the Manganese Dioxide** (Lunge's method).—1·0866 gram of the dry substance is mixed, in a 300 c.c. flask furnished with a Bunsen valve (*see* Limestones and Clays), with 75 c.c. of ferrous sulphate solution (100 grams of the pure sulphate or the corresponding quantity of ferrous ammonium sulphate, and 100 c.c. of conc. pure sulphuric acid in 1 litre), the titre of which has been recently determined with N/2-permanganate (15·815 grams of pure permanganate per litre). The flask is closed and heated until all the pyrolusite is acted on, that is, until no brown deposit remains. When cool, the liquid is diluted with about 200 c.c. of boiled water and titrated with the permanganate solution until the pink coloration persists for half a minute. The difference between the number of c.c. of permanganate used to titrate the 75 c.c. of the ferrous solution and that used in the test gives, when multiplied by 2, the percentage of $MnO_2$ in the substance (1 c.c. of the $KMnO_4 = 0{\cdot}02173$ gram of $MnO_2$).

**3. Determination of the Total Manganese.**—1·0875 gram is treated with conc. hydrochloric acid until evolution of chlorine ceases, the excess of acid being neutralised with pure, precipitated calcium carbonate and concentrated, filtered chloride of lime solution added; after heating for a few minutes the liquid is decolorised by addition of alcohol, drop by drop. The whole of the manganese is then precipitated as dioxide (the filtrate should not turn brown on further addition of chloride of lime). The precipitate is filtered off and washed until the wash-water no longer colours starch-iodide paper, and is then treated with ferrous sulphate as in 2. The manganese is calculated as $MnO_2$.

**4. Carbon Dioxide.**—This is determined as in chalk (*see* Chapter on Cement Materials).

**5. Other Tests.**—For the detection and determination of the various foreign substances (*see* above) the ordinary analytical methods may be followed. Tests are made more particularly for oxides of iron and other metals, lime, baryta, silica and phosphoric acid.

In general, pyrolusite contains 35–85% $MnO_2$ (the purer, well crystallised product may contain about 90%). The qualities to be used for making chlorine should contain, if of German origin, not less than 60% $MnO_2$, or, if of Spanish origin, not less than 70%. Extraneous matters may be present in the following proportions: ferric oxide, up to 30%; alumina, up to 4%; lime, up to 4%; silica, up to 20%; and phosphoric acid, up to 1%. The manganese minerals for the manufacture of glass should be free from coloured oxides (iron, nickel, cobalt, copper); those for the treatment of iron or steel should not contain heavy spar, sulphides, copper, nickel, cobalt or phosphorus, and should be poor in silica.

## MERCURIC CHLORIDE (Corrosive Sublimate)

$HgCl_2 = 270{\cdot}98$ (271)

White crystals or crystalline masses soluble in about 16 parts of water (at 15°), in 2·5 parts of 90% alcohol, or in 14 parts of ether. It may contain as impurities, salts of sodium, manganese, zinc or other extraneous metals, arsenic and calomel. The mercuric chloride, especially in basic preparations of the salt, is determined as in 4.

**1. Impurities in general.**—1 gram, dissolved in 10 c.c. of water and acidified with HCl, is treated with excess of hydrogen sulphide: with the pure salt, a black precipitate and a colourless liquid are obtained, the latter leaving no appreciable residue (alkali or alkaline earth salts, etc.) on evaporation.

**2. Arsenic.**—The sulphide precipitate from 1 is treated with dilute ammonia and filtered; the filtrate should not give a yellow colour or precipitate on acidification with hydrochloric acid.

**3. Calomel.**—1 gram should dissolve completely in alcohol or ether.

**4. Quantitative Determination.**—The estimation of mercuric chloride in sublimate pastilles, cotton wool, gauze and other antiseptic preparations is carried out as follows:

(*a*) IODOMETRIC METHOD. 2–3 grams of the sublimate or pastilles are dissolved in water to 500 c.c. With cotton wool, gauze or other similar material, which usually contains about 0·5% of the chloride, 20–25 grams are digested for some hours with water, pressed out well and washed, the liquid being filtered and made up to 500 c.c. An aliquot part of this solution, containing 0·05–0·10 gram of sublimate, is acidified with a little hydrochloric acid and precipitated in the hot with hydrogen sulphide. The mercuric sulphide is filtered off, washed and introduced, with the paper, into a bottle with ground stopper; a little water (20–25 c.c.), about 5 c.c. of carbon disulphide and excess of N/10-iodine (20–25 c.c. usually suffice) are added, the bottle shaken vigorously and the excess of iodine titrated with N/10-sodium thiosulphate in presence of starch paste.[1] The difference between the number of c.c. of iodine solution added and the number of c.c. of thiosulphate necessary to act on the excess of iodine, gives, when multiplied by 0·01356, the mercuric chloride in the volume of solution taken for the determination.

(*b*) ALKALIMETRIC OR HYDRAZINE METHOD,[2] adapted especially for analysis of corrosive sublimate pastilles or compresses. A pastille is dissolved in a little hot water and to the solution are added 20 c.c. of cold saturated hydrazine sulphate solution previously neutralised to methyl orange, and exactly 10 c.c. of N-sodium hydroxide; the liquid is shaken, left for a few minutes, and filtered, the filter being well washed with hot water and the excess of sodium hydroxide in the filtrate titrated with N/10-

[1] The mercuric sulphide reacts with iodine in potassium iodide solution, thus: $HgS + 2I + 2KI = HgI_2 + 2KI + S$. Carbon disulphide is added in order to dissolve the sulphur liberated in this reaction.

[2] According to Rimini, *Rend. R. Accad. Lincei*, XV, 2, p. 323, and *Boll. chim. farm.*, 1908, p. 145.

sulphuric acid in presence of methyl orange. 1 c.c. N-NaOH = 0·1084 gram $HgCl_2$.

## MERCUROUS CHLORIDE

$Hg_2Cl_2 = 470·9$

A white powder, insoluble in water, alcohol or ether. It is sold as: *Sublimed calomel*, transparent crystals under the microscope; *calomel condensed in steam*, particles which are opaque or at most transparent at the edges; *Precipitated calomel*, formed of very minute, amorphous opaque particles (when the salt is finely triturated, these microscopic characters are no longer discernible). As impurities or adulterants there may appear mercuric chloride, mercuric aminochloride (white precipitate), sodium chloride, barium sulphate, kaolin, lead carbonate, gypsum, chalk, etc.

**1. Fixed Substances.**—1 gram, heated in a porcelain crucible, should yield no appreciable residue if pure.

**2. Mercuric Chloride.**—1 gram is shaken with 10 c.c. of water and filtered, the filtrate being tested with silver nitrate and with hydrogen sulphide; with the former scarcely any milkiness and with the latter a faint brown ccloration are allowable.

**3. White Precipitate.**—The sample is heated with excess of caustic potash solution; in presence of white precipitate, ammonia is evolved.

## CHROME MORDANTS

The chromium compounds used in dyeing and tanning include, besides chromic acid and sodium and potassium chromates and dichromates (*see* separate articles), the following:

*Chromium acetate*, either neutral, $Cr(C_2H_3O_2)_3$, or basic, $CrOH(C_2H_3O_2)_2$, in green or violet solution of 20°, 24° and 30° Baumé or in the dry state. *Chromium Sulphoacetate* and *Nitroacetate*, which are mixtures of the acetate with the sulphate or nitrate of chromium in various proportions.

*Chromium chloride*, in solution of 20–30° Baumé, usually containing basic chlorides, $CrCl(OH)_2$, $CrCl_2(OH)$ and $Cr_2Cl_3(OH)_3$, and often contaminated with alkali salts, sulphates and iron.

*Chromic fluoride*, $CrF_3 + 4H_2O$, in green crystals or powder.

*Chromic formate*, $Cr(HCO_2)_3$ or $CrOH(HCO_2)_2$, in green solution.

*Chromic hydroxide*, $Cr(OH)_3$, in greyish-green paste or powder.

*Chromic sulphate*, $Cr_2(SO_4)_3 + 15H_2O$; *basic sulphates* of various compositions; *chromium and potassium sulphate* or *chrome alum*, $Cr_2(SO_4)_3$, $K_2SO_4 + 24H_2O$, in dark reddish-violet crystals; mixtures in various proportions of more or less basic chromium sulphate with sodium sulphate (often also with the formate) either in green solution or in small green, apparently crystalline fragments. All these sulphates may be contaminated with gypsum, free sulphuric acid and tarry matters.

Analysis of these products includes investigation of the bases and acids

and of any impurities (especially iron), which are detected by the ordinary methods, and especially **determination of the chromium**, for which the two following methods serve :

(*a*) GRAVIMETRIC. The substance (5–10 grams of a solution or 1–2 grams of a solid) is diluted with or dissolved in water (the hydroxide in hydrochloric acid), excess of ammonium chloride or nitrate and slight excess of ammonia being added and the solution boiled until the liquid above the precipitate is quite decolorised. After filtration, the precipitate is washed with water containing ammonium nitrate, dried, ignited and weighed as $Cr_2O_3$ ; 1 part of $Cr_2O_3 = 0{\cdot}6853$ part Cr.

(*b*) VOLUMETRIC. 10 grams of solution (or 1 gram of solid) are dissolved in water or hydrochloric acid and the volume made up to 100 c.c. ; 10 c.c. (= 1 gram of original solution or 0·1 gram of a solid salt) are treated in a litre porcelain dish with concentrated sodium hydroxide solution until the precipitate initially formed redissolves. The dish is then heated on a steam-bath and sodium peroxide added in small amounts until a perfectly yellow solution is obtained (the chromium being transformed into chromate).[1] The liquid is then evaporated to dryness, the residue taken up in water, and the dichromate in the solution estimated iodometrically as described under Potassium Dichromate (5, *b*) : 1 c.c. of N/10-thiosulphate = 0·002533 gram of $Cr_2O_3$.

If the *basicity* of the chromium salt is desired, the acid must be determined and the amount of acid corresponding with 1 part of chromium (*see* Aluminium Sulphate, 3) calculated.

## IRON MORDANTS

These include the sulphate and acetate (*see* separate articles) and solutions of *Basic ferric sulphate* and *Ferric nitrate*, which are known as *iron mordant* or *ferrugine*. These solutions are reddish-brown liquids of D 1·35–1·56, corresponding with 40–52° Baumé, and they contain, besides ferric sulphate or nitrate or both of these salts, also ferrous and alkali salts. These products are analysed as follows :

**1. Nature of the Mordant.**—The dilute solution is treated with hydrochloric acid and barium chloride ; if sulphate is present an abundant white precipitate of barium sulphate is formed. A second portion of the solution is evaporated to dryness on the water-bath and the residue treated with a few pieces of copper and conc. sulphuric acid : if nitrate is present, evolution of red vapours occurs.

**2. Iron.**—10 grams of the substance are diluted to 100 c.c. with water and 10 c.c. of this solution (= 1 gram of substance) boiled with a few drops of nitric acid the iron being then precipitated with ammonia and weighed as ferric oxide, this gives the total iron (1 part $Fe_2O_3$=0·7 part Fe). Another aliquot part of the dilute solution is acidified with pure sulphuric

[1] If the product to be analysed contains organic salts or substances, it should be fused with solid sodium hydroxide (1–2 grams) in a nickel crucible and a small quantity of sodium peroxide then added. After cooling, the mass is dissolved in water and the dichromate in the solution determined iodometrically.

acid and titrated with N/10-permanganate; this gives the iron in the ferrous state (1 c.c. N/10-permanganate = 0·0056 gram Fe).

**3. Sulphuric Acid.**—The filtrate from the total iron precipitate is acidified with hydrochloric acid and precipitated with barium chloride (1 part $BaSO_4$ = 0·3433 part $SO_3$).

**4. Nitric Acid.**—This may be determined by one of the methods given under "Fertilisers."

**5. Alkalies.**—In absence of lime and magnesia (the usual case), it is sufficient to precipitate the iron with ammonia as in 2, to filter, evaporate the filtrate to dryness with a few drops of sulphuric acid, and calcine and weigh the residue: assuming the latter to be sodium sulphate, the alkalies are calculated.

## NITROBENZENE

$C_6H_5{\cdot}NO_2 = 123$

This is sold in various qualities: (1) *Pure light nitrobenzene* (*Essence of mirbane*), a colourless or yellowish liquid with a pleasant odour of bitter almonds, D = 1·208–1·209, b.pt. 205–207°. (2) *Crude heavy nitrobenzene* (*Nitrobenzene for red*), a reddish liquid smelling of bitter almonds and tarry products, D = 1·18–1·19, b.pt. 210–220°; it contains nitrotoluenes and other homologues. (3) *Extra heavy nitrobenzene*, a brownish-red liquid, D = 1·167, b.pt. 220–240°, containing little nitrobenzenes and much nitrotoluenes, nitroxylenes, etc.

With these products the determinations usually made are those of the specific gravity and the boiling point.

*Nitrotoluene* may be detected in pure nitrobenzene by shaking a few c.c. of the product with 1–2 grams of powdered sodium (not potassium) hydroxide: in presence of nitrotoluene, even in very small amounts, the liquid becomes brownish yellow.

Pure nitrobenzene should have a specific gravity not less than 1·20 (at 15°), and at least 95% of it should distil between 204° and 208°.

## POTASSIUM ALUMINIUM SULPHATE—*see* Alum

## POTASSIUM BISULPHITE

$KHSO_3 = 120$

This usually forms slightly effloresced crystalline masses, very readily soluble in water to an acid solution. It may contain the same impurities as sodium bisulphite and its value depends on its proportion of sulphur dioxide. Its analysis is carried out similarly to that of the sodium salt.

Commercial potassium bisulphite is also called *metabisulphite*, and is probably a mixture of the normal bisulphite, $KHSO_3$, and the metabisulphite, $K_2S_2O_5$. It contains about 53% of total $SO_2$.

## POTASSIUM BITARTRATE (Cream of Tartar)

$KC_4H_5O_6 = 188{\cdot}2$

The impure salt constitutes crude tartar (*see* p. 36). The pure or refined product forms white rhombic crystals or crystalline powder and dissolves in about 220 parts of cold water or 15 parts of boiling water, but is insoluble in alcohol.

It may be contaminated with small proportions of calcium, lead, copper or iron salts, or adulterated with various mineral salts (alum or other acid salt). Its analysis includes the following :

**1. Insoluble Substances.**—1 gram is either treated with 220 c.c. of water at the ordinary temperature or boiled with 18 c.c. of water. If the salt is pure, a clear solution should be obtained in either case ; any insoluble residue left is tested especially for calcium tartrate, calcium carbonate, gypsum, clay, etc.

**2. Nitrates, Sulphates, Chlorides.**—10 grams are heated to boiling with 30 c.c. of water, cooled and filtered, the filtrate being tested with the ordinary reagents for these radicles.

**3. Heavy Metals.**—5 grams are dissolved in ammonia, the liquid being acidified with hydrochloric acid and treated with hydrogen sulphide, then with ammonium sulphide, etc., according to the ordinary method of analysis.

**4. Calcium Tartrate** (small quantities).—1 gram is treated in the hot with 10 c.c. of water and a few drops of ammonia until solution occurs : ammonium oxalate should give no turbidity.

**5. Quantitative Determination.**—0·5 gram is dissolved in boiling water (100 c.c.) and titrated with normal alkali in presence of phenolphthalein. 1 c.c. N-alkali = 0·1882 gram of potassium bitartrate.

## POTASSIUM BROMIDE

$KBr = 119$

White, deliquescent crystals, highly soluble in water. It may be contaminated by bromates, sulphates, chlorides, iodides and carbonates. The tests and determinations made are as follows :

**1. Sulphates, Metals, Alkaline Earths.**—The 1 : 10 solution is tested with barium nitrate (sulphates), hydrogen sulphide (heavy metals), ammonia, ammonium sulphide and ammonium oxalate. Sodium is detected by the flame test or by potassium pyroantimoniate.

**2. Carbonates.**—No effervescence should be obtained with dilute hydrochloric acid. A crystal placed on red litmus paper and moistened with a drop of water gives a blue stain if alkali carbonate is present.

**3. Bromates.**—0·1 gram, moistened with very dilute sulphuric acid, should not turn yellow or emit an odour of bromine.

**4. Iodides.**—0·5 gram, dissolved in 5 c.c. of water, is treated with a drop of ferric chloride solution or a few crystals of potassium nitrite and a

few drops of dilute sulphuric acid and shaken with chloroform ; the latter is coloured violet in presence of iodides.

**5. Chlorides.**—0·5 gram is dissolved in 30 c.c. of water and 5 c.c. of this solution, acidified with nitric acid, treated with silver nitrate until precipitation is complete ; the precipitate is washed several times by decantation and then digested with 4 c.c. of ammonium carbonate solution (1 : 6) and filtered : the filtrate, acidified with nitric acid, should give at most a faint milkiness.

**6. Quantitative Determination.**—10 c.c of a solution of 3 grams of the bromide, dried at 100°, in 100 c.c. of water, are titrated with N/10-silver nitrate in presence of potassium chromate. The red colour should be obtained with 25·2 c.c. of the silver solution, if the bromide is pure. If chlorides are present, a larger quantity is required.

The volume permitted by the Italian Pharmacopœia is 25·4 c.c. of the N/10-silver solution.

## POTASSIUM CARBONATE

$K_2CO_3 = 138·2$ (138)

*Crude potassium carbonate* (*crude potash*) forms reddish or bluish grey, spongy masses, deliquescent in moist air. Its impurities are more particularly water, chlorides, sulphates, sulphites, sulphides, phosphates, cyanogen compounds, potassium hydroxide, sodium carbonate and insoluble matter. Its analysis includes determinations of the insoluble matter, carbonate, hydroxide, chloride, sulphate and sulphide (sulphite), which are carried out as in sodium carbonate (*q.v.*), and also of the water, phosphates and sodium salts (*see* below).[1]

*Commercial pure potassium carbonate* (*refined potash*) occurs in powder, or in hygroscopic, white crystalline crusts extremely soluble in water. According to the degree of refining, it may contain more or less marked proportions of chloride, sulphate, phosphate, silicate, insoluble substances and moisture, which are investigated as described under "Caustic Potash," and are determined as in crude potash.

The *chemically pure carbonate* (*puriss.*) should contain only traces of chloride and sulphate and is tested like potassium hydroxide (*q.v.*).

**1. Water.**—10 grams are heated to redness in a platinum crucible, the loss representing water.

**2. Phosphates.**—5 grams are dissolved in nitric acid and filtered, the filtrate being heated and precipitated with ammonium molybdate ; the precipitate is dissolved in ammonia, precipitated with magnesia mixture (*see* Fertilisers) and the magnesium ammonium phosphate filtered, ignited and weighed as magnesium pyrophosphate in the ordinary way. $Mg_2P_2O_7 \times 1·907 = K_3PO_4$.

**3. Sodium Salts.**—10 c.c. of the 10% solution of the carbonate (=1 gram of substance) are exactly neutralised with N-hydrochloric acid (to methyl orange), heated to expel carbon dioxide (and any sulphur dioxide

[1] For the *Rapid Analysis of Potassium Carbonate*, see also E. Baroni in *L'Industria chimica*, 1904, VI, p. 164.

or hydrogen sulphide) and normal barium chloride solution added in amount exactly equivalent to the potassium sulphate (also to any phosphate present) already found by another way. The liquid is heated and filtered, the insoluble matter washed, the filtrate evaporated to dryness and the residue carefully ignited, taken up in a little water and a few drops of ammonium carbonate, the solution filtered if necessary and evaporated in a tared platinum dish, the residue being gently ignited and weighed. In the pure chlorides thus obtained the chlorine is determined volumetrically by Volhard's method and the chlorides of sodium and potassium calculated (*see* Stassfurt Salts, Determination of sodium chloride). A better method (especially if the sodium is in small amount) is to determine the potassium as platinichloride or perchlorate and to calculate by difference the sodium chloride, which is then expressed as carbonate: $NaCl \times 0{\cdot}906 = Na_2CO_3$.

*Crude* potassium carbonate usually contains 50–90% of $K_2CO_3$, with varying proportions of water, insoluble substances, sulphate, chloride, etc. In some crude potashes as much as 60% of sodium carbonate occurs, but the best qualities contain about 2%.

The *commercial pure* carbonate, from Stassfurt salts, contains 96–98% $K_2CO_3$, and the less pure forms from molasses 92% $K_2CO_3$ with more or less considerable proportions of phosphate, often caustic potash and sulphur and cyanogen compounds, and sodium carbonate (0·05–2·5%), potassium chloride (0·5–2·5%), and potassium sulphate (0·5–3%).

The *chemically pure* carbonate may still contain traces of chloride and sulphate.

## POTASSIUM CHLORATE

$KClO_3 = 122{\cdot}56$ (122·5)

Colourless, odourless crystals soluble in about 16 parts of cold water; when heated it fuses and evolves oxygen. It is usually met with in the pure state, but it may contain small quantities of chlorides, hypochlorites, sulphates, arsenic, lead, iron and lime. Adulterations with nitre, potassium chloride, boric acid and mica have been detected. These impurities may be discovered by the following tests and the chlorate determined as in 7.

**1. Chlorides, Sulphates.**—The 1 : 20 solution is tested with silver nitrate or barium chloride.

**2. Hypochlorites.**—The 1 : 20 solution should give no immediate blue coloration with potassium iodide and starch paste in the cold, but the pure chlorate yields a faint blue after some minutes.

**3. Nitrates.**—1 gram, heated with 5 c.c. of sodium hydroxide solution, 0·5 grams of iron turnings and 0·5 gram of zinc dust, should not evolve ammonia.

**4. Metals, Alkaline Earths.**—The 1 : 20 solution is treated with hydrogen sulphide or ammonia and ammonium sulphide or ammonium oxalate: no turbidity should appear.

**5. Arsenic.**—1 gram is strongly heated to transform it into chloride and then tested in the Marsh apparatus (*see* Flesh Foods, Vol. II).

**6. Boric Acid, Mica.**—The sample is treated with 96% alcohol and filtered, the filtrate being tested for boric acid by burning the alcohol (green

flame) and by means of litmus paper (red coloration). The mica is recognised by its insolubility in water.

**7. Quantitative Determination.**—0·1–0·2 gram is distilled with hydrochloric acid and the chlorine absorbed in potassium iodide, the liberated iodine being titrated with thiosulphate solution : 1 c.c. N/10-thiosulphate = 0·0020416 gram $KClO_3$.

## POTASSIUM CHLORIDE

*See* Stassfurt Salts, under Fertilisers

## POTASSIUM CHROMATE

$K_2CrO_4 = 194·2$

Yellow crystals, soluble in water. It is moderately pure as sold, the most frequent impurities being free alkalies and sulphates, detectable as follows :

**1. Free Alkali.**—The aqueous solution, suitably diluted, is tested with a few drops of phenolphthalein.

**2. Sulphates.**—3–5 grams in 100 c.c. of water, acidified with hydrochloric acid, are tested with barium chloride : with the pure salt, no turbidity should be formed even after 12 hours.

**3. Chlorides.**—The dilute solution, heated with nitric acid and silver nitrate, should give no precipitate.

**4. Alumina, Alkaline Earths.**—The 1 : 20 solution is tested with ammonia and ammonium oxalate.

**5. Quantitative Determination.**—*See* Potassium Dichromate.

## POTASSIUM CYANIDE

KCN = 65·11 (65)

White or dirty white powder or fused masses, very readily soluble in water to an alkaline solution and soluble also in alcohol if this is not too concentrated. The usual impurities are carbonates, sulphates, chlorides, sulphides, cyanates, thiocyanates, ferrocyanides and soda. Sometimes it may also contain small quantities of heavy metals, especially iron and lead, and traces of silver. The tests made are as follows :

**1. Solubility.**—1 gram in 10 c.c. of water should give a clear solution, and 2 grams should dissolve at the ordinary temperature in 50 c.c. of 70% alcohol (by weight).

**2. Carbonates.**—The aqueous solution (1 : 10) is treated with lime water, which gives a white turbidity or precipitate in presence of carbonates.

**3. Sulphates.**—The 1 : 10 solution, acidified with hydrochloric acid (***under a hood***), is tested with barium chloride.

**4. Sulphides.**—The 1 : 10 solution is tested with lead acetate : black coloration or precipitate in presence of sulphide.

**5. Cyanates.**—The salt is triturated with about 84% alcohol, filtered and concentrated, and hydrochloric acid added: if cyanate were present, effervescence will occur.

**6. Thiocyanates, Ferrocyanides.**—The 1 : 10 solution is tested with a few drops of ferric chloride, which gives a red coloration with thiocyanates and a blue precipitate with ferrocyanides.

**7. Chlorides.**—1 gram is mixed with 2 grams of nitre and 10 grams of pure potassium carbonate and fused to decompose the cyanide, the fused mass being dissolved in water, acidified with nitric acid and tested with silver nitrate.

**8. Soda.**—1 gram is evaporated to dryness with excess of hydrochloric acid (*in a good draught*), the residue being dissolved in a little water and tested for sodium by the flame or by means of potassium pyroantimoniate.

**9. Heavy Metals.**—The 1 : 10 solution is boiled with hydrochloric acid until all the hydrocyanic acid is expelled (*in a good draught*) and then tested with hydrogen sulphide, with subsequent addition of ammonia.

**10. Quantitative Determination.**—10 grams are dissolved in water and the solution made up to a litre; to 25 c.c. of the solution (= 0·25 gram of substance) are added a crystal of sodium chloride and N/10-silver nitrate then run in from a burette until a persistent turbidity is obtained. The number of c.c. used, multiplied by 5·2, gives the percentage of KCN in the sample.[1]

Chemically pure potassium cyanide contains about 99% KCN; the commercial pure product and that for technical purposes contain considerably less (only up to 50%). The commercial salt often contains marked proportions of sodium cyanide and when this is calculated as potassium cyanide, the content of the latter appears greater than the true value (sometimes even greater than 100%); in such cases the soda may be determined, proceeding as in 8 (above) and then testing the alkali chlorides by the ordinary methods (*see* Fertilisers, Stassfurt Salts).

## POTASSIUM DICHROMATE

$$K_2Cr_2O_7 = 294{\cdot}2$$

Orange red crystals soluble in water. The commercial salt is usually pure or almost so, only containing small quantities of sulphates and of residue insoluble in water. It may, however, contain also chlorides, lime and magnesia and may be adulterated with sodium dichromate (especially when powdered). Its value depends essentially on the content of real dichromate or of chromic anhydride. The analysis includes, therefore, the following tests and determinations:

**1. Sulphates.**—3 grams, dissolved in 100 c.c. of water, acidified with

[1] When silver nitrate acts on potassium cyanide, it gives first the soluble double cyanide of potassium and silver:

$$AgNO_3 + 2KCN = KAg(CN)_2 + KNO_3;$$

as soon, however, as the silver nitrate is in excess, it reacts with the sodium chloride forming insoluble silver chloride.

If the sample contains appreciable proportions of sulphides, titration with silver nitrate is preceded by agitation of the solution with powdered lead carbonate and filtration.

30 c.c. of hydrochloric acid (D 1·12) and treated in the hot with barium chloride, should give no turbidity or precipitate, even after standing.

**2. Chlorides.**—1 gram dissolved in water and acidified with nitric acid, should not be rendered turbid by silver nitrate.

**3. Lime, Magnesia.**—2 grams dissolved in 30 c.c. of water and mixed with 10 c.c. of ammonia (D = 0·96) should be rendered turbid neither by ammonium oxalate nor by sodium phosphate.

**4. Sodium Salts.**—These are detected by the flame, after moistening with hydrochloric acid. Indirectly they are indicated by the content of chromic anhydride (*see* 5).

**5. Determination of the Dichromate.**—This can be carried out in two ways:

(*a*) By Reduction. 5 grams of the dichromate are dissolved in water and the volume made up to 1 litre. 10 c.c. of this solution (= 0·05 gram of substance) are acidified with sulphuric acid, mixed with about 1 gram (weighed exactly) of ferrous ammonium sulphate, the excess of the ferrous salt remaining unaltered being then titrated with N/10-permanganate. The difference between the quantity of iron used, which is given by (grams of ferrous ammonium sulphate) ÷ 7, and that of the iron remaining unchanged (1 c.c. N/10-permanganate = 0·0056 gram Fe) gives the amount of iron required to reduce the 0·05 gram of substance taken: Fe × 0·8781 = $K_2Cr_2O_7$ and Fe × 0·5969 = $CrO_3$.

(*b*) Iodometrically. 5 grams of dichromate are dissolved to 1 litre. To 25 c.c. of the solution (0·125 gram of substance) are added 4–5 grams of potassium iodide, 20 c.c. of 50% sulphuric acid and about half a litre of water, the iodine liberated being titrated with N/10-sodium thiosulphate in presence of starch paste. 1 c.c. N/10-thiosulphate = 0·0049 gram of $K_2Cr_2O_7$ or 0·00333 gram of $CrO_3$.

When the proportion of $CrO_3$ found is greater than the theoretical proportion for pure potassium dichromate (68%), the presence of sodium dichromate is to be inferred.

Commercial potassium dichromate is usually guaranteed to contain 67·5–68% of $CrO_3$.

## POTASSIUM FERRICYANIDE (Red Prussiate of Potash)

$$K_6Fe_2(CN)_{12} = 658·6$$

Reddish-brown, anhydrous crystals soluble in water, insoluble in alcohol. It may contain the same impurities as the ferrocyanide, these being detectable similarly (*see* succeeding article). It may also contain ferrocyanide, detectable as follows:

**1. Ferrocyanide.**—The 1 : 20 solution is treated with a few drops of dilute ferric chloride: if the red prussiate is pure only a faint brown coloration appears, whereas in presence of ferrocyanide a blue coloration or precipitate is formed.

**2. Quantitative Determination.**—The ferricyanide is first reduced to ferrocyanide and this then estimated. 2 grams of the salt are dissolved

in 100 c.c. of water and treated with an excess of caustic potash and then, drop by drop and with shaking, with ferrous sulphate solution until a black precipitate appears; the volume is then made up to 500 c.c., the liquid filtered and the ferrocyanide in 25 c.c. of the filtrate (= 0·1 gram of substance) determined as indicated under Potassium Ferrocyanide (5). From the quantity and titre of the permanganate used the ferricyanide is calculated: $Fe \times 11{\cdot}769 = K_6Fe_2(CN)_{12}$.

If the red prussiate contains ferrocyanide, the latter is determined directly prior to reduction and allowance then made for it in the above calculation.

## POTASSIUM FERROCYANIDE (Yellow Prussiate of Potash)

$$K_4Fe(CN)_6 + 3H_2O = 422{\cdot}4$$

Lemon-yellow crystals soluble in water. The usual impurities may contain small quantities of carbonates, sulphates, chlorides and soda. The tests are as follows:

**1. Carbonates.**—The powdered salt is moistened with dilute hydrochloric acid to see if effervescence occurs.

**2. Sulphates.**—The 1 : 20 solution, acidified with hydrochloric acid, is tested with barium chloride.

**3. Chlorides.**—1 gram is fused with 2 grams of nitre in a porcelain crucible and the mass dissolved in water, acidified with nitric acid and tested with silver nitrate.

**4. Soda.**—The solution of 1-2 grams in 100 c.c. of water is acidified with a little hydrochloric acid and treated with a slight excess of ferric chloride, the liquid being filtered and the excess of iron in the filtrate precipitated with ammonia. The solution is again filtered, the filtrate being concentrated to small volume and tested for sodium by means of potassium pyroantimoniate.

**5. Quantitative Determination.**—10 grams are dissolved in water to 1 litre, 10 c.c. (= 0·1 gram of substance) being diluted in a porcelain dish with about 250 c.c. of water, acidified with dilute sulphuric acid and titrated with permanganate. The ferrocyanide is then calculated from the titre of the permanganate: $Fe \times 7{\cdot}56 = K_4Fe(CN)_6, 3H_2O$.

Commercial yellow prussiate is usually moderately pure, containing at least 99% of $K_4Fe(CN)_6, 3H_2O$.

## POTASSIUM HYDROXIDE (Caustic Potash)

$$KOH = 56{\cdot}1 \quad (56)$$

This is sold in lumps, scales, sticks (ingots) or powder, or in solution and in various degrees of purity, such as *Caustic potash puriss.* or *by baryta*, prepared from the sulphate and from baryta, *Caustic potash pure by alcohol*, *Caustic potash pure by lime*, and *Crude caustic potash*. The impurities it contains vary in nature (especially carbonates, sulphates, chlorides, nitrates,

silica, alumina and ferric oxide) and in proportions. The tests made are as follows :

**1. Solubility.**—10 grams with 20 c.c. of water should give a clear, colourless solution. Any insoluble residue (silica, ferric oxide, etc.) may be filtered off and weighed.

5 grams dissolved in 10 c.c. of water and treated with 25 c.c. of 95% alcohol, should give a clear, homogeneous solution, which does not separate into two layers on standing (carbonates and other salts).

**2. Chlorides.**—2 grams are dissolved in water, acidified with nitric acid and made up to 60 c.c. ; silver nitrate should then cause only a faint opalescence.

**3. Sulphates.**—3 grams are dissolved in 50 c.c. of water, acidified with hydrochloric acid, boiled and treated with barium chloride. Any turbidity or precipitate formed after an hour is observed.

**4. Nitrates.**—2 grams are dissolved in water, neutralised with sulphuric acid and diluted to 25 c.c., this solution being poured carefully into a test-tube containing 10 c.c. of conc. sulphuric acid with a few crystals of diphenylamine : any blue coloration formed at the zone of contact of the two liquids within a few minutes is noted.

**5. Carbonates.**—2 grams are dissolved in 10 c.c. of water and the solution poured into dilute (1 : 1) hydrochloric acid, any effervescence being observed.

**6. Phosphates.**—5 grams, dissolved in water and acidified with nitric acid, are treated with ammonium molybdate and gently warmed : the formation of a yellow precipitate within about two hours is noted.

**7. Silica.**—5 grams are dissolved in dilute hydrochloric acid, the liquid evaporated to dryness, the residue heated at 105°, and taken up in water again : gelatinous flocks separate after some time if silica is present.

**8. Alumina.**—5 grams are dissolved in dilute acetic acid, a slight excess of ammonia being added and the volume made up to 100 c.c. with water : the deposition of gelatinous flocks immediately or within about two hours indicates alumina.

**9. Heavy Metals.**—5 grams, dissolved in slight excess of dilute hydrochloric acid, are treated with hydrogen sulphide and any turbidity noted, either before or after addition of excess of ammonia.

**10. Sodium.**—The solution in hydrochloric acid is tested in the Bunsen flame.

**11. Ammonia.**—2–3 grams are dissolved in water and the solution tested with 2–3 drops of Nessler solution.

**12. Quantitative Determination.**—The total alkalinity and the alkalinity after treatment with barium chloride are determined with methyl orange as indicator, the amounts of potassium hydroxide and carbonate being thus obtained. 1 c.c. N-acid = 0·056 gram KOH or 0·069 gram $K_2CO_3$.

The determination of the various impurities is carried out by methods similar to those indicated under " Sodium Carbonate " (*q.v.*).

***

**The best potassium hydroxide is that termed " by baryta " ; then come that " by alcohol " and that " by lime."**

*Caustic potash by baryta* should contain only traces of chlorides (faint opalescence with silver nitrate) and should not give the reactions for sulphates, nitrates, carbonates, etc. (*vide supra*). Its content in KOH should not be less than 80%, the remainder being water, which is inevitable in the purest products.

In *potassium hydroxide by alcohol* traces of chlorides, sulphates, silica (separation of flocks in test 7) and alumina (few flocks after some hours in test 8) are allowable ; the water should not exceed 20%.

In *potassium hydroxide by lime* small proportions of the above impurities, such as chlorides, sulphates, etc., are tolerated. Its total alkalinity should be not less than 80% and its content of carbonate not more than 5%.

*Crude caustic potash* contains marked amounts of chlorides, sulphides, carbonates, etc. ; its value depends essentially on the proportion of KOH, determined as in 12.

## POTASSIUM IODIDE

$KI = 166{\cdot}12$

White (or faintly yellow if very old) crystals, extremely soluble in water. It may contain bromides, chlorides, iodates, cyanides and the other impurities found in the bromide. The principal impurities are tested for as follows :

**1. Iodates, Carbonates.**—The powdered substance is treated with dilute sulphuric acid ; effervescence indicates carbonates, and yellow coloration, iodates. To 5 c.c. of the 1 : 20 solution are added a few drops of starch paste and 5–6 drops of dilute tartaric acid (1 : 50) ; in presence of iodates, the liquid turns blue.

**2. Chlorides, Bromides.**—About 0·5 gram is dissolved in ammonia, treated with silver nitrate, shaken, filtered, and the filtrate acidified with nitric acid : with chloride or bromide, a precipitate forms.

**3. Cyanides.**—The solution (1 : 20), treated with a crystal of ferrous sulphate, a drop of ferric chloride, eight drops of sodium hydroxide solution and, after gentle heating, acidified with hydrochloric acid, becomes blue if cyanides are present.

**4. Sulphates, Metals, Alkaline Earths.**—*See* Potassium Bromide (1).

Pure potassium iodide for pharmaceutical purposes should contain, according to the Italian Pharmacopœia, neither iodates, carbonates, sulphates, heavy metals, nor cyanides. Test 2 (above) should give at most a faint white or yellowish opalescence.

## POTASSIUM LACTATE

For use in dyeing, an acid lactate of potassium, $KH_5C_3O_3 + H_6C_3O_3$, is sold under the name *Lactolin* as a yellowish-brown, syrupy liquid, containing about 50% by weight of the acid lactate. *Lactolin A* and *Lactolin B* represent the corresponding acid lactates of sodium and ammonium.

The impurities of these products are the same as in lactic acid and are investigated in the same way (*see* Lactic Acid).

The free acid is determined by titration with N-alkali in presence of phenolphthalein and the total acid by oxidation with permanganate, according to Ulzer and Seidel (*see* Lactic Acid).

## POTASSIUM NITRATE

$KNO_3 = 101{\cdot}1$

Large, colourless, rhombic prisms or dry, white crystalline powder, soluble in 4 parts of cold water, insoluble in absolute alcohol. *Crude nitre* may contain various impurities (up to 20%), namely, chlorides, chlorates, perchlorates, sulphates, nitrites, iodates, lime, magnesia, soda, copper, and insoluble substances (sand, earthy matter). In general *refined nitre* is fairly pure, only containing traces of chlorides. The tests to be made are as follows:

**1. Insoluble Substances, Metals, Alkaline Earths, etc.**—5 grams are dissolved in 50 c.c. of water, filtered from any insoluble residue and the filtrate tested with ammonia, ammonium sulphide, ammonium oxalate and sodium phosphate (*see also* Potassium Hydroxide).

**2. Sodium Salts.**—If the nitre does not colour the flame yellow it is free from sodium salts, while if it does give a colour these salts may be present only in traces. The nitre is well and repeatedly triturated with alcohol and the liquid filtered and evaporated: in presence of sodium nitrate, the residue is composed almost exclusively of this salt.

**3. Chlorides, Sulphates.**—The solution (1 : 20) is tested with silver nitrate and with barium chloride: with pure nitre, no turbidity should be observed even after some hours.

**4. Chlorates, Perchlorates.**—Where no chlorides are present, chlorates or perchlorates may be detected by calcining a little of the nitre, dissolving the residue in water acidified with nitric acid and testing with silver nitrate: a turbidity indicates chlorate or perchlorate. If this test gives an affirmative result, and also if the nitre contains chlorides, the chlorates and perchlorates may be determined as follows:

(*a*) 5 grams of the nitre are dissolved in water, filtered if necessary, then slightly acidified with nitric acid and the liquid titrated with silver nitrate and decinormal thiocyanate according to Volhard's method. The chlorine thus found exists as chlorides.

(*b*) 5 grams of the nitre and 10 grams of zinc dust (free from chlorine) are gently boiled for half an hour with 150 c.c. of 1% acetic acid, the liquid being filtered and the chlorine in the filtrate determined. This chlorine is that of the chlorides and chlorates.

(*c*) In a flat platinum dish, 5 grams of the nitre are mixed to a paste with about 1 c.c. of pure, saturated sodium carbonate solution by means of a platinum wire; the paste is then dried over a small flame and heated gradually to redness. When cool, the mass is taken up with water, the solution being acidified with nitric acid and the chlorine again determined: this represents the chlorine of the chlorides, chlorates and perchlorates.

**5. Iodates.**—A solution of 5 grams of the nitre is acidified with dilute sulphuric acid and zinc turnings and a little starch paste added: presence of iodates is indicated by a blue coloration.

**6. Nitrites.**—To the 1 : 10 solution of the nitre are added 6 drops of 1 : 50 sulphuric acid, a little starch paste and 3–4 drops of potassium iodide

solution (1 : 20) free from iodates : in presence of nitrites, a blue coloration is obtained almost immediately.[1]

**7. Quantitative Determination.**—Analogous to that of sodium nitrate (*see* Fertilisers).

Nitre for the manufacture of gunpowder should not, according to French requirements, contain more than 0·033% of sodium chloride ; according to the German, not more than 0·010%, and according to the English and Italian, not more than 0·005%. Further, it should contain only traces of chlorates and perchlorates.

## POTASSIUM OXALATE

Various potassium oxalates exist : *Neutral oxalate*, $K_2C_2O_4 + H_2O$ = 184·2, colourless crystals, soluble in 3 parts of cold water to a neutral solution. The *Acid oxalate* or *bioxalate*, $KHC_2O_4 + H_2O$ = 146·1, in colourless, transparent, rhomboidal crystals, soluble in 25 parts of cold water to an acid solution. The *Quadroxalate* or *Tetroxalate*, $KHC_2O_4$, $H_2C_2O_4 + 2H_2O$ = 254·1, colourless crystals soluble in about 55 parts of cold water to an acid solution. *Salts of Sorrel*, a mixture of the bi- and tetr-oxalate, soluble in 40 parts of water giving an acid solution. In these products the impurities to be tested for are chlorides, sulphates and lead :

**1. Chlorides, Sulphates.**—The solution, acidified with nitric acid, is tested with silver nitrate or barium chloride.

**2. Lead and other Heavy Metals.**—1 gram, dissolved in water and rendered alkaline with ammonia, is treated with ammonium sulphide.

**3. Determination of the Oxalic Acid.**—The *total acid* is determined, either by precipitating as calcium oxalate with ammonia and calcium chloride, and weighing as lime (1 part CaO = 1·607 part $H_2C_2O_4$), or volumetrically with permanganate (1 c.c. N/10-permanganate = 0·0045 gram $H_2C_2O_4$).

The *free acid*, derived from the bioxalate or tetroxalate and used to deduce the nature of the acid salt, is determined by titration with N-alkali in presence of phenolphthalein : 1 c.c. N-alkali = 0·045 gram $H_2C_2O_4$.

1 gram $KHC_2O_4 + H_2O$ requires 6·85 c.c. N-alkali.

1 gram $KHC_2O_4$, $H_2C_2O_4 + 2H_2O$ requires 11·80 c.c. N-alkali.

## POTASSIUM PERMANGANATE

$KMnO_4$ = 158

Violet-red crystals of metallic lustre, soluble in 16 parts of cold water. The tests made are as follows :

**1. Chlorides, Sulphates.**—2 grams are dissolved in 50 c.c. of water and the solution heated with 10 c.c. of alcohol until decolorisation is complete. The liquid is filtered and the filtrate acidified with nitric acid and tested with silver nitrate and with barium chloride.

**2. Nitrates.**—1 gram is dissolved in 10 c.c. of water and the solution, after decolorisation with oxalic acid, mixed with an equal volume of conc.

[1] If the potassium iodide is not absolutely free from iodates, the blue coloration may also appear, at any rate after some time. The test is, of course, invalid if the nitre contains iodates.

sulphuric acid ; when ferrous sulphate solution is poured carefully on to the surface of the liquid, no brown coloration should be formed at the zone of contact.

**3. Quantitative Determination.**—The solution is titrated with ferrous ammonium sulphate or N/10-oxalic acid. To 10 c.c. of N/10-oxalic acid, mixed with 1 c.c. of dilute sulphuric acid (1 : 4), the permanganate solution (3·16 grams per litre) is run in until a persistent pink coloration appears ; with the pure salt, 10 c.c. should be required.

## POTASSIUM PERSULPHATE

(*See under* Ammonium Persulphate)

## POTASSIUM SULPHATE

$K_2SO_4 = 174$

The *crude sulphate* for fertilising purposes (*see* Potassium Salts, under Fertilisers) and the *pure sulphate*, in large, colourless crystals soluble in water, are on the market. The latter may contain small quantities of chlorides, calcium, magnesium and sodium salts, and potassium hydrogen sulphate. These impurities are detected as follows :

**1. Chlorides.**—The solution, acidified with nitric acid, should give no turbidity with silver nitrate.

**2. Metals.**—The solution should not change with ammonium sulphide, ammonia, ammonium oxalate or sodium phosphate.

**3. Sodium Salts.**—These are recognised by the yellow coloration of the flame.

**4. Bisulphate.**—When bisulphate is present, the reaction is acid to litmus paper.

## POTASSIUM SULPHIDE

$K_2S + 5H_2O = 200{\cdot}2$

The ordinary sulphide forms colourless, greenish or yellowish, deliquescent crystals or fused, yellowish-red hygroscopic masses ($K_2S$), and is not much used. More common is a mixture of *Potassium polysulphides* with thiosulphate and sulphate, known as *Liver of sulphur*, which forms deliquescent, greenish-yellow masses, reddish-brown inside, with a sulphurous odour, largely soluble in water and partly so in alcohol (about 50%).

The analysis is carried out as with the corresponding sodium salt (*q.v.*) ; 1 c.c. N/10-zinc sulphate = 0·05 gram $K_2S + 5H_2O$ = 0·02755 gram $K_2S$.

For the analysis of liver of sulphur it is usually sufficient to verify the external characters (the fracture should exhibit a reddish-brown liver colour) and the reactions for polysulphides and potassium (with excess of hydrochloric acid, hydrogen sulphide should be evolved and sulphur deposited ; if the liquid is then boiled and filtered and the filtrate evaporated to dryness,

the residue should give the reactions for potassium in the flame and with tartaric acid).

## SILVER NITRATE

$AgNO_3 = 169{\cdot}94$ (170)

Transparent, colourless crystals, alterable in the light in presence of organic matter, soluble in 0·5 part of water, in alcohol o.· in ether. The tests to be made are :

**1. Solubility.**—1 part, with 0·5 part of water, should give a solution which is clear and remains so after addition of alcohol.

**2. Extraneous Salts.**—1 gram, dissolved in 40 c.c. of water, is treated with 6 c.c. of N-hydrochloric acid ; the silver chloride is allowed to deposit in the hot and the filtered liquid evaporated and the residue ignited gently : no appreciable residue should remain—merely a faint black stain of reduced silver.

## SODIUM ACETATE

$NaC_2H_3O_2 + 3H_2O = 136{\cdot}12$

Colourless crystals extremely soluble in water and in 25 parts of 90% alcohol ; also the anhydrous salt (*Fused sodium acetate*) in greyish, fused masses. The pure salt should answer the following tests :

**1. Reaction.**—The 1 : 10 solution should be clear and should not redden phenolphthalein and should react slightly alkaline with litmus paper.

**2. Empyreumatic or Tarry Substances.**—0·5 gram should dissolve in pure conc. sulphuric acid without browning. 0·5 gram, dissolved in water, acidified with 5 c.c. of pure dilute sulphuric acid (1 : 3) and treated with 1 drop of N/10-permanganate, should have a persistent pink colour

**3. Extraneous Metals.**—The 1 : 10 solution, acidified with hydrochloric acid, should not give a blue colour with potassium ferrocyanide (*iron*) and should not change with hydrogen sulphide (*heavy metals*) ; acidified with acetic acid, it should undergo no change with ammonium oxalate (*lime*) ; acidified with nitric acid, it should give no turbidity, even after standing, with barium chloride (*sulphates*), and with silver nitrate should give at most a slight opalescence (*chlorides*).

## SODIUM ALUMINATE

$Al_2Na_2O_4 = 164{\cdot}2$

This is sold in white crystalline masses, or as a moist paste, or in solution. It is soluble in water but the solution becomes cloudy in the air. The common impurities are insoluble substances, silica and iron (*see* 1–3, below), and the value depends on the content of alumina and sodium oxide (*see* 4).

**1. Insoluble Substances.**—10–20 grams are dissolved in hot water and the solution filtered through a tared filter,[1] the insoluble part being

[1] As it is an alkaline liquid it is best to use a filter of either hardened paper or other similar good filter-paper.

washed, first with hot water, then with dilute hydrochloric acid and finally with water again; it is then dried and weighed.

**2. Silica.**—5–10 grams of the substance are dissolved in hydrochloric acid, the liquid evaporated to dryness, the residue heated at 110–120°, taken up with hydrochloric acid, filtered, washed, ignited and weighed.

**3. Iron.**—This is detected and determined as in aluminium sulphate (*q.v.*).

**4. Determination of the Alumina and Soda.**—Results sufficiently accurate for technical purposes are given by Lunge's method:

20 grams of the aluminate are dissolved in water to 1 litre and 10 c.c. of this solution (= 0·2 gram of substance) boiled and titrated with N/5-hydrochloric acid in presence of phenolphthalein until the latter is decolorised (only the alkali of the aluminate being neutralised). The liquid is then cooled to 30–37°, a drop (not more) of methyl orange added, and the liquid then retitrated with the same acid to an incipient red tint (the aluminium hydroxide liberated in the preceding reaction is then neutralised). From the number of c.c. of acid used in the first titration (phenolphthalein) the soda is calculated (1 c.c. N/5-HCl = 0·00621 gram $Na_2O$) and from the number of c.c. used in the second titration (methyl orange) the alumina is calculated (1 c.c. N/5-HCl = 0·003407 gram $Al_2O_3$).

For more exact determinations phenolphthalein should be added to the aluminate solution, a current of carbon dioxide being then passed through it until the red colour disappears. The precipitated aluminium hydroxide is filtered off, washed, dried, ignited and weighed as $Al_2O_3$. In the filtrate the $Na_2O$ is determined by titration with N/5-hydrochloric acid in presence of methyl orange.

## SODIUM BICARBONATE

$NaHCO_3 = 84·06$ (84)

Crystalline crusts or white powder with slightly alkaline taste, soluble in 12 parts of water. It may contain the same impurities as the normal carbonate but especially ammonium salts (chloride), thiosulphates, arsenites and normal carbonate. The tests to be made are:

**1. Ammonia, Chlorides.**—1 gram should not give off ammonia when heated in a test-tube, and when dissolved in 50 c.c. of water and treated with a few drops of Nessler solution should not colour. With silver nitrate in presence of nitric acid, no more than a slight opalescence should develop in 10 minutes.

**2. Arsenites, Thiosulphates.**—A solution of 1 gram in 50 c.c. of water, acidified with acetic acid and treated with silver nitrate, should not give either yellow (*arsenite*) or brown opalescence (*thiosulphate*).

**3. Normal Carbonate.**—1 gram dissolved in 50 c.c. of cold water without too much shaking, should not turn red on addition of 3 drops of phenolphthalein solution (less than 2% of normal carbonate). Quantitative determination of the carbonate and bicarbonate may be carried out thus:

5 grams are dissolved in about 100 c.c. of cold boiled water without shaking but merely crushing with a glass rod; to the solution about 10

grams of pure sodium chloride are then added and the whole cooled to 0° and titrated with N-hydrochoric acid in presence of phenolphthalein until the red coloration disappears (1 c.c. N-acid = 0·053 gram $Na_2CO_3$). Methyl orange is next added and the titration continued with the same acid to a red colour (1 c.c. N-acid = 0·084 gram $NaHCO_3$).

## SODIUM BISULPHATE

$NaHSO_4+H_2O=138$

Colourless crystals or white, fused masses, soluble in water to an acid solution. It may contain the same impurities as the sulphate and these are detected by similar methods (*see* Sodium Sulphate). The content of pure sodium bisulphate is determined thus.:

**Quantitative Determination.**—4–5 grams are dissolved in water and titrated with normal alkali (methyl orange) : 1 c.c. N-alkali = 0·120 gram $NaHSO_4$ or 0·0138 gram $NaHSO_4 + H_2O$.

## SODIUM BISULPHITE

$NaHSO_3 = 104·1$ (104)

This is put on the market in crystals, or moist crystalline masses, or dry white powder, or solution ; the crystals and the dry powder are usually odourless, but the other qualities smell of sulphur dioxide. It is soluble in water giving an acid solution.

It may contain the same impurities as the neutral sulphite and these are similarly detected (*see* Sodium Sulphite) ; iron and sulphate especially should be tested for. Its value depends essentially on the content of bisulphite or sulphur dioxide (free ; semi-combined, that is, as bisulphite ; combined, that is, as normal sulphite), which is determined as follows :

**Quantitative Determination.**—This is based on the facts that the total sulphur dioxide may be estimated by titration with iodine and that the free or semi-free sulphur dioxide reacts acid towards phenolphthalein, whereas the semi-free has a neutral reaction towards methyl orange. In other words : with phenolphthalein only the normal sulphite reacts neutral, while with methyl orange the bisulphite also reacts neutral ; free sulphur dioxide is acid towards both indicators.

(*a*) TOTAL SULPHUR DIOXIDE.—5 grams are dissolved to 1 litre in recently boiled and cooled water, this solution being run from a burette into 15 c.c. N/10-iodine solution in a flask until the liquid is almost decolorised ; starch paste is then added and the titration continued until the blue colour disappears : 1 c.c. N/10-iodine = 0·0032 gram $SO_2$.

(*b*) FREE AND SEMI-FREE SULPHUR DIOXIDE.—200 c.c. of the solution prepared as in (*a*) are titrated with N-sodium hydroxide in presence of methyl orange until a yellow coloration is attained ; this gives the free $SO_2$ (1 c.c. N-alkali = 0·064 gram $SO_2$). Phenolphthalein is then added and the N-sodium hydroxide run in until a red colour appears ; this gives the semi-free $SO_2$ (1 c.c. N-alkali = 0·032 gram $SO_2$). These two values

together, when subtracted from the total sulphur dioxide, give that existing as normal sulphite.

Commercial solid sodium bisulphite, sometimes called also *Metasulphite* or *Pyrosulphite* (*see* Potassium bisulphite), usually contains 60–62% of total $SO_2$; the solution of 38–40° Baumé contains 24–25%.

## SODIUM CARBONATE

$Na_2CO_3 = 106$; $Na_2CO_3 + 10H_2O = 286$

This is sold as: *Crude sodium carbonate* (*Crude soda*), in more or less coloured, crystalline masses, contaminated by chlorides, sulphates, sulphides, thiocyanates, phosphates, silica, heavy and earthy metals and sodium hydroxide; *Crystallised carbonate* (*Soda crystals*) with 10 mols. of water, containing particularly sulphates and chlorides but not in large proportions; *Dry carbonate* (*Calcined soda* or *Soda ash*) in white powder or masses, which may contain sulphate, sulphide and hydroxide if made by calcination of Leblanc soda, or chloride and bicarbonate, if it is Solvay or ammonia soda. There is also *pure sodium carbonate* (crystallised or dry), which should be free from impurities.

The analysis of sodium carbonate includes the qualitative investigation of the various impurities (tests 1–14), to be made particularly on the pure and chemically pure products; and the determination of the water, titre and some of the commoner impurities, especially with commercial sodas (15–17). The quantities given for tests 1–9 refer to the crystallised carbonate; one-third as much of the anhydrous carbonate should be taken.

1. **Solubility.**—1 gram in 10 c.c. of water should give a clear solution.

2. **Sulphates, Chlorides.**—5 grams, dissolved in a slight excess of dilute nitric acid and the solution made up to 25 c.c. with water, are tested with barium chloride in the hot—examining after standing for 12 hours (*sulphates*)—or with silver nitrate (*chlorides*).

3. **Nitrates.**—*See* Caustic Potash.

4. **Phosphates.**—20 grams dissolved in dilute nitric acid are treated with ammonium molybdate at a gentle heat.

5. **Silica.**—20 grams are dissolved in dilute hydrochloric acid and evaporated on a steam-bath, the residue being dried at 105° and taken up in water: the solution thus obtained should be clear and should not deposit flocks even after long standing.

6. **Arsenic.**—The solution is tested in the Marsh apparatus for one hour.

7. **Alumina.**—10 grams dissolved in 50 c.c. of water are acidified with acetic acid, and then rendered alkaline with ammonia: any formation of gelatinous flocks after long standing is noted.

8. **Heavy Metals.**—10 grams are dissolved in water (50 c.c.), acidified with dilute hydrochloric acid and treated with hydrogen sulphide: no change should occur even after addition of ammonia in excess.

9. **Potassium.**—3 grams, dissolved in dilute hydrochloric acid, are treated with a few drops of platinic chloride and the liquid evaporated on a steam-bath; the dry residue should give a clear solution in 50 c.c. of 80% alcohol.

**10. Ammonia.**—*See* Caustic Potash.

**11. Sodium Hydroxide.**—3 grams, dissolved in 50 c.c. of water, are treated with 6 grams of crystallised barium chloride, dissolved in 50 c.c. of water and the solution shaken and filtered. The filtrate gives a red coloration with phenolphthalein if sodium hydroxide is present. For the quantitative determination, *see* 17 (below).

Traces of caustic alkali are readily detected also by moistening the sample with a few drops of *Dobbin's reagent* (yellow coloration). This reagent is prepared by adding to an aqueous solution of 5 grams of potassium iodide a solution of mercuric chloride until a permanent precipitate just appears; after filtration, 1 gram of ammonium chloride is added and then dilute sodium hydroxide solution until a precipitate is formed; after filtering again, the volume is made up to 1 litre.

**12. Sodium Bicarbonate.**—A few grams are heated at about 250° in a test-tube with a delivery-tube dipping into lime water: the latter becomes turbid if bicarbonate is present. Quantitative determination is made as with Sodium bicarbonate (3).

**13. Sodium Sulphide.**—The 1 : 10 solution is either treated with sodium nitroprusside solution (violet coloration) or acidified with dilute hydrochloric acid and tested with lead acetate paper (brown coloration). For quantitative determination, *see* 17 (below).

**14. Sodium Sulphite.**—The 1 : 10 solution, containing a little starch paste, is acidified with acetic acid and tested with dilute iodine solution (decoloration). For quantitative determination, *see* 17 (below).

**15. Determination of the Moisture** (in calcined or Solvay soda).—5 grams are heated for 30 minutes at 300° in a platinum crucible immersed in a sand-bath, cooled in a desiccator and weighed.

**16. Determination of the Strength.**

(*a*) CRYSTALLISED SODA. 5 grams are dissolved in water to 1 litre, 50 c.c. of this solution (= 2·5 grams of substance) being titrated in the cold with N-hydrochloric acid (methyl orange). 1 c.c. N-HCl = 0·053 gram $Na_2CO_3$ = 0·143 gram $Na_2CO_3 + 10H_2O$.

(*b*) CALCINED SODA. Either of two methods may be used.

1. *English Method.* 26·5 grams of substance are dissolved in hot water, the liquid being made up when cold to 500 c.c. and, if necessary, filtered; 50 c.c. of the filtrate (= 2·65 grams of substance) are titrated in the cold with N-HCl in presence of methyl orange: 1 c.c. N-acid = 2% of $Na_2CO_3$.

2. *German Method* (Lunge's conditions, adopted by the German soda manufacturers). 2·65 grams of substance, previously dehydrated, are dissolved in water and the unfiltered solution titrated with N-HCl in presence of methyl orange: 1 c.c. N-acid = 2% of $Na_2CO_3$.

The value of the soda is expressed in *degrees*, expressing the content in sodium carbonate or in sodium oxide. French or Gay-Lussac degrees, and also English degrees, give the percentage of $Na_2O$ in the commercial soda; English degrees are, however, slightly greater than the French, the equivalent of sodium oxide being taken as 32 instead of 31. German degrees give the content of $Na_2CO_3$. Lastly, French Descroizilles degrees indicate the grams of monohydrate sulphuric acid ($H_2SO_4$) necessary to neutralise 100 grams of the soda. Thus, 1

Gay-Lussac degree = 1·01 English degree = 1·71 German degree = 1·58 Descroizilles degree.

**17. Complete Analysis.**—100 grams of the soda are dissolved in a beaker in hot water and the liquid allowed to stand in the hot for half an hour, after which it is filtered through a filter dried at 100° and tared, the insoluble matter being washed with hot water and used for determination (*a*). The filtrate is collected in a litre flask and made up to the mark on cooling, being used for the determinations (*b*) to (*h*).

(*a*) INSOLUBLE RESIDUE. The insoluble matter, dried at 100°, is weighed. It is then moistened with water, lixiviated with hot, dilute hydrochloric acid (which dissolves the ferric oxide, alumina, calcium and magnesium carbonates), washed with water, redried at 100° and weighed; this represents sand and carbon (%). After ignition the sand is weighed alone and the carbon then obtained by difference.

(*b*) TOTAL ALKALINITY AND SODIUM CARBONATE. 10 c.c. of the solution (= 1 gram of substance), diluted with water, are titrated in the cold with N-HCl (methyl orange). This gives total alkalinity, due to carbonate, hydroxide and sulphide; deduction from the volume of acid used of those corresponding to the hydroxide and sulphide (determinations *c* and *d*) and multiplication of the remainder by 53 gives the grams of $Na_2CO_3$ per 100 grams of the soda.

(*c*) SODIUM HYDROXIDE. 100 c.c. of solution (= 10 grams of substance) are shaken in a 200 c.c. flask with excess of barium chloride (10 c.c. of 10% solution usually suffice), made up to volume, again shaken and left to stand; 100 c.c. of the clear liquid (not filtered) are pipetted off and titrated with N-hydrochloric acid in presence of phenolphthalein. This gives alkalinity due to hydroxide and sulphide together; subtraction of the corresponding number of c.c. from determination (*d*) and multiplication of the remainder by 0·8 gives percentage of NaOH.

(*d*) SODIUM SULPHIDE. 50 c.c. of solution (= 5 grams of substance) are heated to boiling, treated with ammonia and ammoniacal silver nitrate solution (13·82 grams Ag per litre) [1] run in from a burette until no further black precipitate is produced. To determine the end-point the more readily, the liquid is filtered towards the end of the titration and the latter continued in the filtrate. The number of c.c. of silver solution, multiplied by 0·1, gives the percentage of $Na_2S$ in the sample. 1 c.c. of silver solution = 0·13 c.c. of N-acid (for calculations indicated in *b* and *c*).

(*e*) SODIUM SULPHITE. 50 c.c. of the solution (= 5 grams of substance) are acidified with acetic acid and titrated with N/10-iodine in presence of starch paste. The number of c.c. used, multiplied by 0·1261, gives the percentage of $Na_2SO_3$ in the sample.

When sulphides are present, the number of c.c. of iodine solution used must be diminished by that corresponding with the sulphide found as in (*d*), knowing that 1 c.c. of silver solution = 1·3 c.c. N/10-iodine.

(*f*) SODIUM CHLORIDE. With ammonia soda, 20 c.c. (= 2 grams of

[1] 13·82 grams of pure silver are dissolved in nitric acid, 250 c.c. of ammonia being added and the liquid diluted to 1 litre. 1 c.c. of this solution = 0·005 gram $Na_2S$.

substance) or with Leblanc soda, 50 c.c. (= 5 grams) of solution are neutralised exactly with N-nitric acid, the liquid boiled, 10 drops of 10% potassium chromate solution added, and N/10-silver nitrate run in from a burette until a red coloration appears. 1 c.c. N/10-silver nitrate = 0·005846 gram NaCl.

(*g*) SODIUM SULPHATE. With Leblanc soda, 50 c.c. (= 5 grams of substance) or with ammonia soda, 100 c.c. (= 10 grams) of the solution are acidified with hydrochloric acid, heated to boiling, precipitated with barium chloride, filtered and the barium sulphate washed, dried, calcined and weighed: 1 gram of $BaSO_4$ = 0·6089 gram of $Na_2SO_4$.

(*h*) SILICA AND ALUMINA. 100 c.c. of the solution (= 10 grams of substance) are acidified with hydrochloric acid and evaporated on a water-bath, the residue being dried at 105° and taken up in hydrochloric acid; the silica is separated and weighed, and the alumina estimated in the solution in the ordinary way.

***

Commercial *soda crystals* should contain at least 34% of $Na_2CO_3$; usually they contain 35% (theoretically 37·042% $Na_2CO_3$ and 62·958% $H_2O$). Sometimes a slight excess of water is present, but this should not exceed 1%; often slight efflorescence is shown. The ordinary impurity is sulphate (in Leblanc soda; *see* later), but large proportions, such as 10–20%, must be regarded as added artificially. The chloride content in Leblanc soda should not exceed 0·5%. The yellowish colour of certain soda crystals is usually derived from organic substances and not from iron.

*Calcined Leblanc soda* may contain small proportions of hydroxide, sulphide and sulphite, and is often contaminated with sulphate; its strength may vary from 80 to 96%, but is most often 88–95%. *Ammonia soda* contains chloride, and sometimes small quantities of bicarbonate; its strength is 95–98%.

The moisture of calcined soda is usually 0·5–1%, 3% being tolerated; in moist air, calcined soda may absorb up to about 10% of moisture.

The insoluble substances in ordinary good soda should not exceed 0·5%, of which about 0·1% is insoluble in hydrochloric acid and 0·02% ferric oxide.

The sulphate in ammonia soda should not be more than 0·1%, if not added. In Leblanc soda of best quality 0·5–1% occurs, while in inferior qualities it reaches 8% or more.

The chloride occurs to the extent of 0·5–2·5% in ammonia soda or 0·25–0·5% in Leblanc soda.

*Pure* or *chemically pure sodium carbonate* should answer all the qualitative tests, 1–14.

## SODIUM CHLORATE

$NaClO_3$ = 106·5

White crystals or powder soluble in about 1 part of cold water. The commercial product does not reach the degree of purity of potassium chlorate, but usually contains small quantities of chlorides, lime and, sometimes, iron. The various impurities and also the content of chlorate are investigated and determined as in potassium chlorate (*q.v.*): 1 c.c. N/10-thiosulphate = 0·001775 gram $NaClO_3$.

## SODIUM CHLORIDE

$NaCl = 58{\cdot}46$ (58·5)

This is sold in various degrees of purity, the most common impurities being: potassium and magnesium chlorides, sodium, calcium and magnesium sulphates, insoluble substances (sand, clay) and sometimes small quantities of bromides, iodides, borates and lithium salts

Analysis includes, therefore, tests for the above and any other impurities (1–6) and, if the exact composition of the salt is to be known, certain quantitative determinations (7).

**1. Solubility and Various Impurities.**—1 gram in 10 c.c. of water should give a clear, neutral solution.

The 1 : 10 solution is tested with hydrogen sulphide (*heavy metals*), ammonium sulphide (*iron, zinc*), ammonium chloride, ammonia and ammonium oxalate (*lime*) and, after removal of any lime present, with sodium phosphate (*magnesium*).

**2. Potassium Salts.**—These are detected in the flame through cobalt glass, or by dissolving 1 gram of substance in a little water, adding platinic chloride, evaporating on a steam-bath, taking up with 50 c.c. of 80% alcohol, any yellow, crystalline precipitate formed immediately or after some hours being observed.

**3. Lithium Salts.**—A few grams of the finely powdered salt are moistened with 90% alcohol and filtered, the filtrate being examined in the flame (through cobalt glass) or better through a spectroscope.

**4. Sulphates.**—The 1 : 10 solution is treated with barium chloride in the hot and the liquid examined after standing.

**5. Iodides, Bromides.**—5 grams are moistened with a little water and filtered; to the filtrate are added a crystal of sodium nitrite and acetic acid, the whole being then shaken with carbon disulphide, which becomes violet or yellowish in presence of iodides or bromides respectively.

**6. Boric Acid.**—25 grams are heated, with occasional shaking, with about 50 c.c. of 95% alcohol acidified with hydrochloric acid and filtered, the filter being washed with a little alcohol and the filtrate rendered alkaline with sodium hydroxide and evaporated on a steam-bath. The residue is taken up with a little dilute hydrochloric acid and the solution tested with turmeric paper (better, paper immersed in 0·1% alcoholic turmeric solution), which is then dried at 100° (reddening).

**7. Quantitative Determinations.**—(*a*) MOISTURE. 5 grams of the salt are heated for 3–4 hours in a dry, tared conical flask of about 250 c.c. capacity, with a funnel inserted in the neck, on a sand-bath at 140–150°. The flask is then allowed to cool in the air on a marble slab and reweighed.

(*b*) INSOLUBLE SUBSTANCES. 10 grams of the salt are dissolved in water, the solution being filtered through a filter dried at 100° and tared The insoluble matter is washed with nearly half a litre of water, dried at 100° and weighed. The filtrate is made up to 500 c.c. and used for the following determinations.

(*c*) CHLORINE. 50 c.c. of this solution (= 1 gram of salt) are titrated with silver nitrate in the usual way. 1 c.c. N/10-$AgNO_3$ = 0·355% Cl.

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(*d*) SULPHURIC ACID. 150 c.c. of the solution (= 3 grams of the salt) are acidified with hydrochloric acid and precipitated with barium chloride, the barium sulphate being filtered, washed, dried and weighed as usual: $(BaSO_4 \times 34{\cdot}335) \div 3 = \%$ of $SO_3$.

(*e*) LIME AND MAGNESIA. 150 c.c. of the solution (= 3 grams of salt) are treated with ammonia [1] and ammonium oxalate, the calcium oxalate being ignited and the lime weighed: $(CaO \times 100) \div 3 = \%$ of CaO.

The filtrate from this determination is treated with ammonium or sodium phosphate and the precipitate treated as usual: $(Mg_2P_2O_7 \times 36{\cdot}036) \div 3 = \%$ of MgO.

(*f*) POTASH. 50 c.c. of the solution (= 1 gram of salt) are treated as indicated under "Stassfurt Salts" for the determination of alkalies, the percentages of $Na_2O$ and $K_2O$ being calculated.

(*g*) CALCULATION OF THE RESULTS. The sulphuric acid is combined first with lime, then with magnesia, and lastly, if any remains, with potash and then soda: any remaining magnesium is united with chlorine and the rest of the latter with potash and then with soda.

***

*Chemically pure sodium chloride* should not contain any of the above impurities.

The *pure* and *refined salts* may contain respectively 97–98% and about 99·7% NaCl, and always give the reactions of sulphates and calcium salts; as a rule they contain traces only of magnesium salts.

*Common Salt* (for domestic purposes) varies in composition roughly between the following limits:

| | |
|---|---|
| Sodium chloride | 87–96·4% |
| Magnesium chloride | Traces–1·4% |
| Magnesium sulphate | Traces–1·6% |
| Calcium sulphate | 0·3–1·0% |
| Sodium sulphate | 0–1·2% |
| Water | 0·1–10·0% |
| Impurities (insoluble residue, etc.) | Traces–0·25% |

Incrustations from salt-pans, known as *grofo*, contains less sodium chloride (77–85%) than ordinary salt and also marked proportions of calcium sulphate (up to about 8%), sodium sulphate (up to 8·4%)and magnesium sulphate (2%).

Common salt generally contains small quantities of boric acid, this being particularly the case with certain salts of Italian origin.

In *salt for soap-boiling*, 1% of insoluble impurities and 2% of earthy salts (calcium and magnesium chlorides and sulphates) are allowed by the Union of Italian Soapmakers (1911).

## SODIUM DICHROMATE

$$Na_2Cr_2O_7 + 2H_2O = 298{\cdot}3 \quad (298)$$

The pure salt forms hygroscopic, red crystals, which lose their water of crystallisation at 100°. The dehydrated salt is also sold in large quantities in fused masses or crusts, which are contaminated mainly with sodium sulphate and insoluble carbonaceous substances. Its value depends on its content of chromic anhydride. The following tests are made:

[1] If the ammonia produces a precipitate (iron, aluminium), this is filtered off and *washed and the filtrate* then treated as described.

**1. Insoluble Substances.**—A few grams are dissolved in water and the solution filtered through a tared filter, which is then treated in the ordinary way.

**2. Water.**—2–3 grams are heated at 100–105° to constant weight.

**3. Sulphates.**—Tested for as in potassium dichromate (*q.v.*) and determined as barium sulphate.

**4. Determination of the Chromic Anhydride.**—As with potassium dichromate (*q.v.*).

Pure crystallised sodium dichromate contains 67% of $CrO_3$, and the anhydrous salt 76·4%. The fused commercial product usually contains 73–74% $CrO_3$.

## SODIUM HYDROXIDE (Caustic Soda)

$NaOH = 40$

This is sold in lumps, sticks or powder, and in various degrees of purity (*Caustic soda from sodium, by alcohol, by lime, purified, crude*). The commonest impurities, often in considerable quantities, are carbonates, sulphates, chlorides, nitrates, alumina, ferric oxide and lime; these are detected as in caustic potash.

The strength is determined by measuring the total alkalinity and the alkalinity after treatment with barium chloride (methyl orange used) as indicated under " Sodium carbonate " : 1 c.c. N-acid = 0·04 gram NaOH or 0·031 gram $Na_2O$ or 0·053 gram $Na_2CO_3$.

***

*Sodium hydroxide pure from metal* represents the best quality sold, and should contain only traces of chlorides and at most 5% of water.

*Sodium hydroxide by alcohol* should answer the same requirements as potassium hydroxide by alcohol, and should not contain more than 5% of water.

In *sodium hydroxide by lime* the total alkalinity should not be less than 90% and the content of carbonate not greater than 5%.

The strength of caustic soda for soap works is usually expressed as $Na_2O$ (1 c.c. N-acid = 0·031 gram $Na_2O$). In that of 60–65 strength, 3% of carbonate is allowable and in that of 70–77 strength, 1·5% of carbonate.

## SODIUM NITRATE

*See* Fertilisers

## SODIUM NITRITE

$NaNO_2 = 69$

This is sold in white or yellowish crystals or cast rods and is extremely soluble in water and moderately so in alcohol. It usually contains very few impurities and its value depends essentially on the content of $NaNO_2$.

**Quantitative Determination** (Lunge's method).—A seminormal permanganate solution is prepared by dissolving 15·82 grams of chemically pure potassium permanganate in water to 1 litre, the titre being controlled

by iron or by oxalic acid (1 c.c. = 0·028 gram Fe = 0·0315 gram crystallised oxalic acid).

10 grams of the nitrite are dissolved in water to 1 litre. 20 c.c. of the permanganate solution are mixed in a conical flask with about 130 c.c. of water and a little dilute sulphuric acid and the liquid heated to 40–50°, the nitrite solution being then run in from a burette until the colour disappears. 1 c.c. N/2-$KMnO_4$ = 0·01725 gram $NaNO_2$, so that 20 c.c. = 0·3450 gram, and the percentage of nitrite is given by $3450 \div n$, where $n$ is the number of c.c. of nitrite solution used.

Commercial sodium nitrite generally contains 97–99% of $NaNO_2$.

## SODIUM PERBORATE

$NaBO_3 + 4H_2O = 154$

White powder or colourless crystals, slightly soluble in cold but readily in hot water with liberation of oxygen; with sulphuric acid it gives hydrogen peroxide. Its value depends essentially on the content of actual perborate or active oxygen, which is determined with permanganate as in barium peroxide (*q.v.*). 1 c.c. N/5-permanganate = 0·01483 gram of $NaBO_3 + 4H_2O$ = 0·0016 gram of oxygen.

Commercial sodium perborate is usually guaranteed to contain 10% of active oxygen (theoretically 10·4%).

## SODIUM PEROXIDE

$Na_2O_2 = 78$

Hygroscopic white or yellowish powder, decomposed by water with evolution of oxygen. It may contain, as impurities, sodium hydroxide and carbonate, sulphates, chlorides, phosphates, iron and alumina, which may be detected by the tests indicated under "Potassium Hydroxide." Its value depends on the content of $Na_2O_2$, which may be determined sufficiently exactly for technical purposes by titration with permanganate (*see* Barium Peroxide), but the peroxide must be added to the sulphuric acid with great care. 1 c.c. N/5-permanganate = 0·0078 gram $Na_2O_2$.

An exact determination may be made by Archbutt and Grossmann's method, which consists in decomposing the peroxide with water in presence of a little cobalt nitrate and measuring the volume of oxygen evolved, Lunge's nitrometer or gas-volumometer or similar apparatus being used.[1]

Commercial sodium peroxide (well stored) contains on the average 95% of $Na_2O_2$; its content in $Fe_2O_3 + Al_2O_3$ should not exceed 0·01%.

## SODIUM PHOSPHATE (Disodium Phosphate)

$Na_2HPO_4 + 12H_2O = 358·3$

Colourless, readily efflorescent, more or less large crystals, soluble in water to a faintly alkaline solution. The commoner impurities are car-

[1] *See Analyst*, 1895, p. 3; *Chem. Zeitung*, 1905, p. 138.

bonates, chlorides, sulphates and arsenic (tests 1–4). The content in phosphate may be deduced from the determination of the phosphoric acid (5).

1. **Solubility.**—1 part in 10 of water should give a clear, colourless solution.

2. **Carbonates.**—Any evolution of gas noted on dropping a few crystals into dilute hydrochloric acid.

3. **Chlorides, Sulphates.**—The 1 : 10 solution, acidified with dilute nitric acid, is tested with silver nitrate or barium chloride.

4. **Arsenic.**—1 gram, with 5 c.c. of Bettendorf's reagent, should give no coloration within an hour.

5. **Determination of the Phosphoric Acid.**—25 grams are dissolved in water to 1 litre and in 20 c.c. of this solution (= 0·5 gram of substance) the phosphoric acid precipitated with magnesia mixture (*see* Fertilisers : Determination of Phosphoric Acid, *A*) and the magnesium pyrophosphate weighed as usual : 1 gram $Mg_2P_2O_7$ = 3·216 grams $Na_2HPO_4 + 12H_2O$ = 0·6376 gram $P_2O_5$.

Commercial sodium phosphate of good quality contains about 98% $Na_2HPO_4 + 12H_2O$ or 19·4–19·5% $P_2O_5$.

## SODIUM SILICATE (Water Glass)

This has no well defined and constant composition, but usually consists of a mixture of sodium tri- and tetra-silicates, $Na_2Si_3O_7$ and $Na_2Si_4O_9$. It is sold as a colourless, yellowish or greenish solution (30–33°, 37–40° or 50° Baumé), or in powder or glass-like masses. It dissolves in water (the solid, containing a large excess of silica, only with difficulty), the aqueous solution giving a gelatinous precipitate of silica with acids.

In either the liquid or solid form, chlorides, sulphates, alumina and insoluble substances should be tested for, and the silica and alkali determined :

1. **Solubility.**—20 grams diluted to 500 c.c. should give a clear liquid which does not become turbid after some days.

2. **Chlorides, Sulphates.**—1–2 grams, diluted with 100 c.c. of water, acidified with nitric acid and filtered, is tested with silver nitrate or barium chloride.

3. **Alumina, Ferric Oxide, etc.**—2 grams are evaporated with excess of conc. hydrochloric acid and the residue dried at 120° to render the silica insoluble. The residue is taken up in dilute hydrochloric acid, the solution filtered and the filtrate tested for aluminium, iron, and any lime or other extraneous substance.

4. **Quantitative Determinations.**—100 grams are diluted with water to 1 litre and the solution used for the following determinations :

(*a*) TOTAL ALKALI. 50 c.c. (= 5 grams of substance) are titrated with N-hydrochloric acid in presence of methyl orange : 1 c.c. N-acid = 0·031 gram $Na_2O$.

(*b*) SILICA. 50 c.c. (= 5 grams of substance) are decomposed with conc. HCl in a platinum dish, the liquid being evaporated to dryness, the residue

heated for about 2 hours at 110–120°, treated with dilute hydrochloric acid, and the silica filtered off, washed, dried, ignited and weighed.

In the hydrochloric acid, the alumina, sodium chloride, etc., may be determined.

(*c*) FREE ALKALIES. To 100 c.c. of the solution (= 10 grams of substance) are added, in a thin stream and with constant shaking, 100 c.c. of 10% barium chloride solution, the liquid being made up to 250 c.c., shaken and filtered through a dry paper. The first 20–30 c.c. of the filtrate are rejected and in 100 c.c. of the remainder (=4 grams of substance) the free alkali is titrated with N/10-hydrochloric acid in presence of phenolphthalein : 1 c.c. N/10-acid = 0·004 gram NaOH.

*Potassium silicate* is analysed similarly.

In commercial sodium silicate of good quality the ratio of $Na_2O$ to $SiO_2$ is about 3 : 1, while free alkali is found only in small quantity (less than 0·5%) and the extraneous impurities do not total 2%.

## SODIUM STANNATE

$$Na_2SnO_3 + 3H_2O = 267$$

Hard white crystals or crystalline masses, somewhat efflorescent, soluble in water (in the air the solution becomes cloudy owing to formation of oxide of tin), insoluble in alcohol. Its commoner impurities are sodium carbonate, hydroxide, chloride and sulphate, and iron. Double salts, consisting of sodium stannate and arsenate, or sodium tungstate and stannate, are also sold. Analysis includes the following :

**1. Solubility.**—1 gram, with 10 c.c. of water, should give a clear or barely opalescent solution.

**2. Sodium Carbonate and Hydroxide.**—A few fragments, dropped into dilute hydrochloric acid, should give no effervescence (*carbonate*), and if the substance is dissolved in a little water and then shaken with absolute alcohol, the liquid should not have an alkaline reaction (*hydroxide*).

**3. Chlorides, Sulphate, Iron.**—2 grams are dissolved in 10 c.c. of water, acidified with nitric acid and filtered : the filtrate is tested with silver nitrate (*chlorides*), barium chloride (*sulphates*) and ammonium thiocyanate (*iron*).

**4. Sodium Arsenate.**—1 gram is heated in a porcelain dish with 5 c.c. of nitric acid (1 : 1) on a steam-bath and evaporated to dryness, the residue being taken up in water and a few drops of nitric acid and the liquid filtered. To the filtrate is added an excess of silver nitrate, the liquid again filtered if necessary and very dilute ammonia poured carefully on to the clear filtrate : in presence of arsenate, a reddish ring forms at the zone of contact of the two liquids.

**5. Sodium Tungstate.**—1–2 grams are dissolved in 10 c.c. of water and the liquid filtered and treated with excess of hydrochloric acid : in presence of tungstate a yellowish white gelatinous precipitate is formed which becomes blue when heated gently with a very small quantity of zinc dust.

**6. Determination of the Alkali.**—10 grams are dissolved in water

to 100 c.c. ; 10 c.c. of the solution (=1 gram of substance) are titrated with N-alkali in presence of methyl orange : 1 c.c. N-alkali = 0·031 gram $Na_2O$.

If the total $Na_2O$, thus obtained, is diminished by the quantity corresponding with the stannic oxide found (1 part of $SnO_2$ requires 0·4106 part of $Na_2O$), the free alkali is obtained.

**7. Determination of the Tin.**—1 gram is dissolved in water and hydrochloric acid, the solution being then allowed to react with a few pure aluminium turnings for about half an hour in the cold. The liquid is then heated with a further quantity of conc. hydrochloric acid in a current of carbon dioxide until the spongy tin which has separated completely redissolves ; the subsequent procedure is as indicated under " Stannous Chloride " (quantitative determination).

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Commercial sodium stannate is never completely soluble in water, but it is required to dissolve to as great an extent as possible. The percentage of tin may vary from 30 to 44 (theoretical, 44·85), equal to 38–56% $SnO_2$. The content in free alkali may be variable (up to 5%), as also may the proportions of chloride, sulphate, arsenate and tungstate (commercial stannates have been met with containing 2–50% of sodium chloride and 15–20% of arsenate).

For dyeing purposes, absence of iron and little free alkali are particularly required.

## SODIUM SULPHATE

$Na_2SO_4 + 10H_2O = 322$ ; $Na_2SO_4 = 142$

The pure salt forms colourless crystals (+ $10H_2O$), soluble in about 3 parts of cold water. The crude salt for technical purposes is also sold and forms white or yellowish anhydrous powder or fused masses. The more common impurities are : sodium chloride and bisulphate, magnesium, calcium and ammonium salts, arsenic, heavy metals and insoluble substances. For the analysis of the crystallised salt it is usually sufficient to test for the above impurities by the methods indicated under " Potassium Sulphate " (the arsenic test is made on 1 gram dissolved in 3 c.c. of water, which should not give a brown coloration with 5 c.c. of Bettendorf's reagent within an hour). With the crude salt, the following determinations are made :

**1. Moisture.**—2–3 grams are gently ignited and reweighed.

**2. Free Acid** (*bisulphate*).—20 grams are dissolved in water to 250 c.c., 50 c.c. of the solution (= 4 grams of substance) being titrated with N-alkali in presence of methyl orange : 1 c.c. N-alkali corresponds with 1% $SO_3$.

**3. Sodium Chloride.**—50 c.c. of the solution (= 4 grams of substance) are neutralised exactly with N-alkali (the quantity necessary is known from test 2), a little potassium chromate added and the liquid titrated with N/10-silver nitrate. Each c.c. of N/10-$AgNO_3$ corresponds with 0·146 % NaCl.

**4. Iron.**—10 grams are dissolved in water and the solution treated with sulphuric acid and pure zinc, the iron thus reduced being titrated with permanganate in the ordinary way. If the iron is present in very small proportion, the colorimetric method used with aluminium sulphate may be employed.

**5. Insoluble Substances.**—10–20 grams are dissolved in a little water, the insoluble matter being filtered off, washed, dried, ignited and weighed.

**6. Alumina.**—The filtrate from the preceding operation is heated with a little ammonium chloride and ammonia quite free from carbonate, the precipitate being filtered off, washed, dried, ignited and weighed as $Al_2O_3 + Fe_2O_3$. The proportion of iron being known from determination 4, that of the alumina may be calculated.

**7. Lime.**—The filtrate from the alumina is precipitated with ammonium oxalate, the calcium oxalate being weighed in the usual way as calcium oxide.

**8. Magnesia.**—To the filtrate from the preceding operation (somewhat concentrated if necessary), ammonia and sodium phosphate are added; after 24 hours the precipitate is filtered off, washed with slightly ammoniacal water, dried, ignited and weighed as magnesium pyrophosphate: 1 part of the latter = 0·36242 part of MgO.

**9. Quantitative Determination of the Sodium Sulphate.**—1 gram of the sulphate, dissolved in water, is treated with ammonia and ammonium carbonate to precipitate alumina, iron and lime, the liquid being then filtered and the filtrate evaporated to dryness with a few drops of pure sulphuric acid in a tared platinum dish; the residue is ignited, at first alone and later with a few crystals of pure ammonium carbonate, and weighed. The weight is diminished by that of the sodium sulphate corresponding with the sodium chloride found (in 3) (1 part NaCl = 1·2136 $Na_2SO_4$) and by that of the magnesium sulphate corresponding with the magnesia found (in 8) (1 part MgO = 2·9836 $MgSO_4$); the remainder gives the $Na_2SO_4$ present in 1 gram of substance.

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Crystallised sodium sulphate should contain 44·1% $Na_2SO_4$ and 55·9% $H_2O$, but usually it is somewhat effloresced and the percentage of water rather low; the commonest impurity is a small amount of the chloride.

The crude anhydrous sulphate generally contains 1–2% of moisture, its free acidity being often above 1% and the content of iron usually 0·03–0·15%, but sometimes 0·5% (0·15% is allowable); the proportions of insoluble matter, sodium chloride, alumina, lime and magnesia vary.

## SODIUM SULPHIDE

$$Na_2S + 9H_2O = 240$$

Deliquescent, colourless or more often greenish or yellowish crystals, extremely soluble in water. The calcined (anhydrous) product is also sold in grey or brown, irregular masses soluble in water. The most frequent impurities are: carbonaceous particles, ferric sulphide, sodium thiosulphate and sulphate and free alkali (tests 1–3); the content of $Na_2S$ is found as in 4.

**1. Solubility.**—5 grams should give a clear solution in 50 c.c. of water. If it does not do so (presence of *carbon, ferric sulphide*), the liquid is filtered through a filter previously dried at 105° and tared and the insoluble matter washed well with tepid water, dried at 105° and weighed.

**2. Thiosulphate, Sulphate.**—2 grams are dissolved in a little water *and treated with* excess of dilute hydrochloric acid, any turbidity indicating

*thiosulphate*; the hydrogen sulphide is then expelled by boiling and the liquid, first filtered if necessary, tested with barium chloride (*sulphate*).

**3. Free Alkali.**—5 grams are dissolved in water and titrated with N/10-hydrochloric acid in presence of phenolphthalein: 1 c.c. N/10-acid = 0·0040 gram NaOH.

**4. Determniation of the Sodium Sulphide** (Battegay's method). —50 grams are dissolved in water to 1 litre and 50 c.c. of this solution (= 2·5 grams of substance) neutralised with acetic acid towards phenolphthalein (disappearance of the red colour) and then titrated with N/2-zinc sulphate (71·8425 grams $ZnSO_4 + 7H_2O$ per litre) until a drop of the liquid no longer forms a yellow spot when placed on thick absorbent paper (not ordinary filter-paper) steeped in concentrated cadmium sulphate solution: 1 c.c. N/2-zinc sulphate solution = 0·06 gram $Na_2S + 9H_2O$ = 0·0195 gram $Na_2S$.

Commercial crystallised sodium sulphide is usually pure, or almost so, but the calcined product contains more or less marked proportions of insoluble residue, thiosulphate, sulphate and free alkali.

## SODIUM SULPHITE

$$Na_2SO_3 + 7H_2O = 254$$

Colourless crystals soluble in 4 parts of cold water to a neutral solution. It may contain carbonates, bisulphites, thiosulphates, sulphates, chlorides, and traces of iron and arsenic (tests 1–7). Its value depends on the content of sulphite (8).

**1. Carbonates.**—If sodium carbonate is present, the aqueous solution has an alkaline reaction towards litmus paper, and addition of lime water yields a white turbidity or precipitate.

**2. Bisulphites, Thiosulphates.**—In presence of bisulphite the solution is acid. If thiosulphate is present, sulphur is separated on addition of hydrochloric acid.

**3. Sulphates.**—The solution is boiled with excess of HCl to expel sulphurous acid and tested with barium chloride. It is very difficult to obtain the sulphite free from traces of sulphate.

**4. Chlorides.**—The solution is boiled with excess of nitric acid and tested with silver nitrate.

**5. Arsenic.**—5 grams are evaporated to dryness with pure conc. $H_2SO_4$ and the residue dissolved in water and tested in the Marsh apparatus or with hydrogen sulphide.

**6. Iron.**—The 1 : 10 solution is boiled with a few drops of conc. $HNO_3$, then diluted somewhat and tested with ammonium thiocyanate.

**7. Metals, Earths.**—In absence of metals and alkaline earths, the solution should show no change with ammonium sulphide, ammonia, ammonium oxalate or sodium phosphate.

**8. Quantitative Determination.**—*See* Sodium Bisulphite.

## SODIUM THIOSULPHATE (Hyposulphite)

$Na_2S_2O_3 + 5H_2O = 248{\cdot}3$

Colourless crystals, soluble in water to a neutral solution. It may contain sulphides, sulphates, sulphites, carbonates and chlorides.

**1. Sulphides.**—With lead acetate the solution gives an immediate black coloration or precipitate in presence of sulphide.

**2. Sulphates, Sulphites, Carbonates.**—A solution of 1 gram in 30 c.c. of water should not be rendered turbid by barium chloride or give a red coloration with phenolphthalein (*sodium carbonate*).

**3. Chlorides.**—The 1 : 10 solution is boiled with excess of nitric acid, filtered and tested with silver nitrate.

**4. Quantitative Determination.**—20 grams are dissolved to 1 litre and 20 c.c. of the solution (= 0·4 gram of substance) titrated with N/10-iodine in presence of starch paste : 1 c.c. N/10-iodine = 0·0248 gram $Na_2S_2O_3 + 5H_2O$.[1]

## SODIUM TUNGSTATE

$Na_2WO_4 + 2H_2O = 330$

Colourless crystals or white or yellowish powder soluble in about 4 parts of cold water, and often containing excess of alkali. Its value depends essentially on the content of tungstic acid, which may be determined as follows :

**Determination of the Tungstic Acid.**—1–2 grams are dissolved in a little water and any excess of alkali neutralised with nitric acid in presence of phenolphthalein, conc. mercurous nitrate solution being then added until no further formation of precipitate takes place. After thorough shaking and heating to cause the mercuric tungstate to settle well, the liquid is filtered and the precipitate washed with dilute mercurous nitrate solution, dried at 100°, ignited (under a hood on account of the mercury vapour evolved) and weighed as tungstic anhydride : 1 part $WO_3$ = 1·4224 parts of $Na_2WO_4 + 2H_2O$.

## STANNIC CHLORIDE

$SnCl_4 = 261$ ; $SnCl_4 + 5H_2O = 351$

This is sold as : *Anhydrous stannic chloride*, heavy, colourless liquid emitting dense white fumes in the air, D = 2·26, b.pt. 115° ; *Liquid stannic chloride*, colourless or yellowish aqueous solution of the anhydrous salt, 50–60° Baumé ; *Solid stannic chloride* ($SnCl_4 + 5H_2O$) in white or yellowish, hygroscopic crystalline masses.

The commonest impurities consist of free chlorine, nitric and sulphuric acids, stannous chloride, stannic oxide, ammonium, lead, iron and alkali salts (especially NaCl).

[1] *See also* Sodium Bisulphite.

**1. Impurities in general.**—When the aqueous solution is treated with hydrogen sulphide and filtered, the filtrate should leave no appreciable residue on evaporation.

**2. Free Chlorine.**—The 1 : 10 solution is treated with iodide-starch paste.

**3. Sulphuric Acid.**—The 1 : 10 solution is tested with barium chloride, the barium sulphate being weighed if necessary.

**4. Nitric Acid.**—The concentrated solution is tested with sulphuric acid and ferrous sulphate.

**5. Stannous Chloride.**—The 1 : 10 solution is tested with mercuric chloride (white or grey precipitate). Quantitative determination as under " Stannous Chloride."

**6. Stannic Oxide** (Metastannic Acid).—This is indicated by an insoluble white deposit in the liquid chlorides. The solid chloride (1–2 grams) is treated with excess of sodium hydroxide, which will dissolve it completely in absence of the oxide.

**7. Ammonia.**—The 1 : 10 solution is boiled with excess of sodium hydroxide.

**8. Lead.**—The precipitate formed by hydrogen sulphide (test 1) is treated with yellow ammonium sulphide : in presence of lead an insoluble black residue remains.

**9. Iron.**—The 1 : 10 solution, acidified with HCl, is tested with a few drops of potassium thiocyanate (red coloration).

**10. Alkali Salts** (Sodium Chloride).—These are detected by test 1. For quantitative determination, 1 gram of substance is dissolved in about 500 c.c. of water and the liquid boiled to complete decomposition of the stannic chloride into the oxide and filtered, the precipitate being washed and the total filtrate evaporated to dryness, dried at 120° and weighed.[1]

**11. Determination of the Tin and Hydrochloric Acid.**—1 gram of substance is boiled with 500 c.c. of water as in test 10.[1] The insoluble part is collected on a filter, washed, dried, ignited and weighed as $SnO_2$. 1 part $SnO_2$ = 0·78808 part of Sn.

The filtrate is titrated with N-alkali in presence of phenolphthalein. 1 c.c. N-alkali = 0·0365 gram HCl or 0·0355 gram Cl.

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Stannic chloride of good quality should contain only small proportions of the above impurities. The content of $SO_3$ should not exceed 0·04%, and iron should be only in traces. The solid chloride should contain not less than 45·4% Sn. Sodium chloride often occurs to the extent of 5% or more.

The so-called *Tin Compounds* or *Solutions, Tin mordants, Nitromuriates* or *Sulphomuriates of Tin* consist of solutions of stannic and stannous chlorides with varying proportions of sulphuric and nitric acids, ammonium, zinc or iron salts, sodium chloride, etc. ; their value depends mainly on the proportion of total tin present.

[1] If stannous salts are present, a little bromine water is added prior to the boiling.

## STANNOUS CHLORIDE

$SnCl_2 + 2H_2O = 226$

White or yellowish crystals, soluble in water, alterable in moist air. It may contain, as impurities, oxychloride (insoluble), iron, etc. (*see* Stannic Chloride), and may be adulterated with sodium chloride or sodium, magnesium or zinc sulphate. These impurities are detected as in stannic chloride (tests 1, 3, 7, 8 and 9). The presence of *oxychloride* is indicated by the incomplete solubility of the salt in water and in alcohol.

Its value depends essentially on the proportion of tin in the stannous condition, determinable as follows:

**Quantitative Determination** (Goppel and Fränkel's method).—3–4 grams of the chloride are dissolved in 30–40 c.c. of 10% hydrochloric acid and the liquid diluted to 500 c.c., 50 c.c. of the solution being then treated, in a bottle with a ground stopper, with 50 c.c. N/10-$K_2Cr_2O_7$. After 15 minutes, 10–15 c.c. of potassium iodide solution and 5–10 c.c. of hydrochloric acid (both 1 : 10) are added, and, after a further half an hour, the liquid is diluted with 200 c.c. of water and the iodine liberated titrated with N/10-thiosulphate and starch paste. The difference in c.c. between the volumes of dichromate and thiosulphate, multiplied by 0·0113 gives the amount of $SnCl_2 + 2H_2O$, and multiplied by 0·00595 the amount of tin in the quantity of substance taken for titration.

Stannous chlorides of 99–100% and of 96·8–98·7% are now sold, the latter being guaranteed to contain 51–52% Sn. Adulteration with zinc or magnesium sulphate is now rare.

## SULPHUR

S = 32·07 (32)

Native or *mineral sulphur*, consisting of sulphur mixed with varying proportions of gangue (chalk, gypsum, clay, bituminous matter), is the raw material from which the bulk of the sulphur of commerce is derived. The latter is divided into: *Crude sulphur* of 1st, 2nd and 3rd qualities, in lemon-yellow loaves, which are more or less shining, pale and opaque according to the grade; *Refined sulphur*, in loaves, sticks or powder (*Ground and sieved sulphur*), bright lemon-yellow and shining; *Sublimed sulphur* or *Flowers of sulphur*, a fine, light, yellowish powder. Further, *Magister of sulphur* or *precipitated sulphur* (obtained by treating calcium sulphide solution with hydrochloric acid), for pharmaceutical uses, forms a very fine, light, amorphous powder of dirty yellowish-white colour; finally, *Coppered sulphur*, for agricultural uses, is a mixture of winnowed sulphur with 0·5–5% (usually 3–5%) of copper sulphate.

For certain purposes (manufacture of sulphuric acid), iron *pyrites* may be regarded as a sulphur mineral and will be considered here. These *substances are examined* as follows:

## 1. Sulphur Mineral

The essential determination is that of the sulphur content. The sample should be as representative as possible of the bulk and should be at least 5 kilos, this being finely powdered and well mixed.

**Determination of the Moisture and of the Sulphur.**—5–10 grams are heated in a porcelain dish at 100° to constant weight ; the loss represents moisture. The dry sulphur is then placed in a filter-paper cartridge (finger) and extracted with pure carbon disulphide (free from residue) in a Soxhlet apparatus. The solution is evaporated carefully (carbon disulphide being inflammable) and the residue dried at 70–80° and weighed. This gives the sulphur content provided that the mineral contains no appreciable amount of bituminous substances.

The latter are soluble in carbon disulphide and yield a brown or blackish deposit on the walls and bottom of the vessel (*see* Crude sulphur, 1). In such case the sulphur in the extract is determined by one of the following methods [1] :

(*a*) FRESENIUS AND BECK'S METHOD. This method requires at least 10 grams of residue (sulphur and bitumen) from the carbon disulphide extract.

8–10 grams of the residue are weighed into a porcelain crucible glazed inside and outside, this crucible being then placed inside a second only slightly larger, immersed to its rim in a sand-bath. The temperature of the sand is then maintained at 200–220° for 7–8 hours and the crucible weighed when cool. After a further hour's heating, the crucible is again weighed, this being repeated until no loss of weight occurs.

The loss of weight at 200° represents the sulphur. The residue in the crucible is then ignited until all carbonaceous matter disappears, the new loss of weight giving the bitumen.

(*b*) MANZELLA AND LEVI'S METHOD. This method requires a conical flask of about 100 c.c., with a ground-in air-condenser tube 40 cm. long and 6 mm. bore, the whole being of Jena glass.

0·2 gram of the residue from the carbon disulphide extraction is weighed into the flask, the tube fitted into place and the flask immersed in cold water. Through the inclined tube, 10 c.c. of fuming nitric acid (D = 1·52) and 5 drops of bromine are introduced and the flask shaken until most of the sulphur and bromine are dissolved, 5 c.c. of fuming nitric acid being then added and the flask again shaken for some time. The flask is then heated gently (the water not boiling) in a water-bath for about half an hour. The flask is again immersed in the cold water and 50 c.c. of cold water added, by the tube, drop by drop to avoid any violent evolution of red vapourt. The solution is then transferred to a porcelain dish together with the washings of the flask and tube and evaporated to a small volume, a few drops of conc. hydrochloric acid being added and the liquid again evaporated. The residue is taken up in water and made up to 400–500 c.c. in a beaker, the solution being heated to boiling with 1 c.c. of conc. hydrochloric acid and 5% barium chloride solution in slight excess added drop by drop and with

[1] M. G. Levi : "Methods of *Analysis of* Sulphur" (*Ann. di chim. applic.*, 1915, 1, p. 9).

stirring. The precipitate is collected on a double filter, washed, dried, ignited and weighed as usual.[1] $BaSO_4 \times 0{\cdot}1374 = S$.

## 2. Crude Sulphur.

Crude sulphur is examined for the presence of bitumen, while the moisture and sulphur are determined.

In order to obtain a representative sample, each of a number of the loaves or lumps is broken into 6–8 parts and from each part a slice cut from top to bottom. so that the proportions of sulphur, bitumen and extraneous substances are maintained in each slice. This is of great importance for loaves containing so-called oil or metal (veining or brown layers) or adulterated with earthy matter. From 5 to 10 kilos are taken, pulverised and passed through a silk sieve, the coarser particles being re-ground and again sieved until the whole is in fine powder, which is thoroughly mixed.

**1. Bitumen.**—A little of the sample is heated in a tube and any carbonaceous residue noted. Another way is to dissolve the sample in carbon disulphide and allow the filtered liquid to evaporate spontaneously in a small crystallising dish : in presence of bitumen, a brownish or dark brown border forms on the walls of the vessel and when all the solvent vanishes, crystals of sulphur remain with brown tufts at the salient points.

**2. Determination of the Moisture.**—5 grams of the sample are heated in a tared porcelain dish at 100° in a steam-oven for 1–2 hours (according to some, at 70–80° for 1 hour), the loss representing moisture.

**3. Determination of the Sulphur.**—The dried sulphur is next carefully heated until the sulphur is completely evaporated, the loss then giving the sulphur. If the sample contains bitumen, the sulphur must be determined by the method described for mineral sulphur.

These methods may be applied directly to good sulphurs which leave only traces of residue on ignition, but where appreciable mineral residue remains, the residue from the carbon disulphide extraction is employed.

## 3. Refined Sulphur (loaves or powder)

In refined sulphur in loaves or powder (ground, winnowed) the residue on calcination is determined to check the purity. With sulphur ground and sifted for agricultural purposes, the degree of fineness must be determined.

**Determination of the Degree of Fineness.**—This is effected by Chancel's so-called *Sulphurimeter* or *Sulphinimeter*, which consists of a glass tube with a ground stopper : the tube is 230 mm. long and is graduated from 0 to 100 for a space corresponding exactly with 25 c.c. at 17·5°. The

[1] To eliminate possible errors due to impurities in the reagents and to allow for the filter-ash, a blank determination may be carried out as follows : 25 c.c. of the nitric acid (D = 1·52) and 5 drops of bromine, diluted with a little water, are evaporated almost to dryness on a water-bath, the whole of the nitric acid being expelled by evaporating twice with conc. hydrochloric acid. The residue is taken up in water, a little barium chloride added and the liquid again evaporated almost to dryness, filtered through a double filter, the latter washed with hot water, dried, ashed and weighed. The weight of this residue is subtracted from that of the barium sulphate obtained in *the actual determination* of the sulphur.

length of the tube to the 100 mark is 175 mm., that of the straight tube from the 10 mark to the 100 is 154 mm., and the bore of the tube 12·68 mm.

Into this tube are introduced 5 grams of the sulphur (which should be passed through a sieve of 1 mm. mesh) and about one-half of the ether necessary for the determination, this being absolutely anhydrous and alcohol-free, D = 0·719 at 15°. By gentle tapping the air is completely displaced, more ether being then added to about 1 cm. beyond the 100 mark. The apparatus is placed in a water-bath kept exactly at 17·5° ; after some time the tube is shaken vigorously for 30 seconds and returned to the bath, note being made of the scale-division reached by the sulphur suspended in the ethereal liquid : this division represents the *degree of fineness* of the sample. If the temperature is 2° above or below 17·5°, the result is raised or lowered by 1 degree of fineness and the necessary correction must be made.

The result of the first agitation is too high, so that the determination is repeated several times. After the second or third shaking, the results usually differ by not more than 2 and the mean of two concordant results is taken. Greater certainty is attained by carrying out the test in duplicate.

### 4. Sublimed Sulphur (Flowers of Sulphur)

This form of refined sulphur is in yellow powder composed mostly of agglomerated, microscopic globules mixed with rhombic crystals (ground sulphur being composed solely of crystals or crystalline fragments). It is not completely soluble in carbon disulphide (thus differing from ground sulphur), at least 12% and, in fresh samples, sometimes more than 30% remaining undissolved. When it is moistened with water, the latter may become acid owing to the presence of traces of sulphuric acid.

With sublimed sulphur for agricultural purposes, the residue on calcination and the degree of fineness (*see* Refined Sulphur) are determined ; if for pharmaceutical purposes, arsenic is tested for.

**Detection of Arsenic.**—2 grams are digested for 24 hours with 5 c.c. of 10% ammonia and the solution filtered, acidified with hydrochloric acid and saturated with hydrogen sulphide : in presence of arsenic the liquid becomes yellow.

### 5. Magister of Sulphur (Precipitated Sulphur)

Pale yellow, almost colourless, insipid, impalpable powder. The tests to be made are : residue on calcination, which should be inappreciable ; treatment with dilute hydrochloric acid, which should not cause effervescence, while the filtered liquid should not be rendered turbid by sodium carbonate (alkaline-earth carbonates) ; digestion with water, which should not become acid ; test for arsenic (*see* Sublimed Sulphur).

### 6. Coppered Sulphur

In this product the copper sulphate is determined by repeatedly agitating 10 grams with 200–250 c.c. of hot, acidified water, filtering, washing with boiling water and estimating the copper by one of the methods given under "Copper Sulphate."

## 7. Pyrites

Pyrites or *Iron Pyrites* is a natural ferric sulphide containing, when pure, 53·33% S and 46·67% Fe ; it is, however, usually mixed with gangue and with other minerals, especially of copper, arsenic, cobalt, nickel and, not infrequently, silver and gold.

*Chalcopyrite* or *Copper Pyrites* is a double sulphide of copper and iron, containing in the pure state 34·89% Cu, 30·54% Fe and 34·57% S ; it is often accompanied by iron pyrites and other minerals.

The value of pyrites depends essentially on the proportions of sulphur and copper (2 and 3, below). Other determinations usually made are those of moisture, arsenic and lead (1, 4 and 5).

**1. Moisture.**—10 grams of coarsely powdered pyrites are kept in an oven at 105° until of constant weight (4–5 hours generally suffice).

**2. Sulphur** (Lunge's method).—0·5 gram of pyrites, finely powdered in an agate mortar and sieved through a silk sieve, are treated with 10 c.c. of a mixture of 3 vols. of nitric acid (D 1·4) and 1 vol. of hydrochloric acid (free from sulphuric acid) in a conical flask furnished with a funnel, this being heated on a water-bath so long as brown particles remain unattacked (if any sulphur is unacted on, a few potassium chlorate crystals are added). The liquid is then transferred to a porcelain dish—the flask and funnel being well washed—and evaporated to dryness, the residue being treated with 5 c.c. of conc. HCl and evaporated to dryness again. The residue is then taken up with 1 c.c. of conc. HCl and 100 c.c. of boiling water, the solution being filtered through a small filter and the latter well washed.[1]

The filtrate is neutralised with ammonia (D = 0·91) and then heated for 15 minutes at 60–70° (not to boiling) with addition of 5 c.c. of the same ammonia. The liquid, which should still smell distinctly of ammonia, is filtered at once and the precipitated ferric hydroxide washed rapidly with boiling water until the filtrate ceases to give turbidity with barium chloride, even after standing for some minutes. The filtrate, which should occupy about 300 c.c., is neutralised with pure dilute hydrochloric acid (towards methyl orange), heated to boiling with 1 c.c. of conc. hydrochloric acid and precipitated with a boiling solution of barium chloride (20 c.c. of 10% solution usually suffice). After standing, the clear liquid is decanted through a filter, the precipitate washed 3 or 4 times by decantation with boiling water and transferred to the filter, washed, calcined and weighed : 1 part $BaSO_4$ = 0·13734 S.

**3. Copper** (method used att he Duisburg Mines).—5 grams of extremely finely powdered pyrites dried at 100° are treated in a conical flask with 60 c.c. $HNO_3$ (D = 1·20). When the action is at an end, the liquid is evaporated to dryness and the residue heated until fumes of sulphuric acid appear, the liquid being heated with 50 c.c. of conc. HCl and 2 grams of sodium hypophosphite dissolved in 5 c.c. of water. After addition of more hydrochloric acid and dilution with about 300 c.c. of water, the liquid is treated

[1] The insoluble residue may be dried, calcined and weighed: it contains the silica, *silicates*, barium and lead sulphates, which may occur in small amounts in pyrites. If *the insoluble residue* is very small in quantity, the filtration may be omitted.

with hydrogen sulphide and filtered and the precipitated copper sulphide, with any lead, bismuth and antimony sulphides, rapidly washed. The precipitate is then dropped into a conical flask and redissolved in nitric acid, with which the filter is well washed. The solution is evaporated to dryness and the residue taken up in water and a little nitric acid, neutralised with ammonia, and dilute sulphuric acid added to precipitate the lead. The liquid is then filtered and the insoluble residue well washed, the filtrate being treated with 3–8 c.c. of nitric acid (D 1·40) and subjected to electrolysis to separate the copper. The weight of copper found is diminished by 0·01 gram to allow for any bismuth and antimony present.

Another method, more convenient and rapid, is as follows :

Five grams of the very finely ground pyrites are carefully calcined in a porcelain dish at a dull red heat and are mixed until completely roasted (the arsenic is expelled and the tin rendered insoluble), the product being boiled for 15 minutes with 30 c.c. of nitric acid (D 1·42) in a 250 c.c. flask. When cool, the liquid is made up to the mark with water, shaken and filtered, 200 c.c. of the filtrate (= 4 grams of substance) being neutralised with ammonia, mixed with 5 c.c. of conc. nitric acid and subjected to electrolysis (*see* Copper Sulphate, 3, *a*).

With chalcopyrite and products containing more than 15% Cu, 2 grams are taken for analysis.

**4. Arsenic** (Reich and McCay's method).—0·5 gram is heated almost to dryness with conc. nitric acid in a porcelain basin, 4 grams of sodium carbonate being then added and the evaporation continued to dryness. The residue is then fused and kept fused for 10 minutes with 4 grams of nitre. When cold, the mass is taken up in hot water and the liquid filtered, acidified with nitric acid, boiled to expel all the carbon dioxide, treated with silver nitrate and neutralised with dilute ammonia. The precipitate, which contains all the arsenic as silver arsenate, is filtered off, washed well with water and redissolved in dilute nitric acid, the solution being evaporated to dryness in a tared platinum basin. The residual silver arsenate is either weighed or titrated with thiocyanate according to Volhard's method for determining silver : 1 part of $Ag_3AsO_4$ = 0·162 part of As ; 1 part of Ag = 0·2315 part of As.

**5. Lead.**—The insoluble residue remaining after the treatment with aqua regia for the determination of sulphur (*see* 2) is treated with a hot, concentrated ammonium acetate solution, the liquid evaporated to dryness with a little sulphuric acid, and the lead sulphate—thus separated from other insoluble matter—ignited and weighed : 1 part $PbSO_4$ = 0·6832 part Pb.

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Sicilian *Mineral sulphur* may contain up to about 90% of sulphur, but high proportions (above 40%) are rare. Those containing 30–40% are usually regarded as rich, 20–30% as good, 15–20% as ordinary, and less than 15% as poor. Most of it is yellow tending to grey or greenish, but some is brown owing to bitumen. Those of Romagna contain, on the average, 10–20%, and occasionally 30% of sulphur, and are often bituminous. Those of Louisiana are very rich (60–98%), while those of Nevada, Utah, Texas, etc., contain varying proportions (15–80%).

*Crude sulphur* usually *contains* 98–99·5% of sulphur. The moisture rarely

reaches 0·1% and the extraneous matters (mineral substances, bitumen) vary mostly from 0·5 to 1%, but sometimes reach 2%.

*Refined sulphu* and *Sublimed* or *Flowers of sulphur* should contain only negligible amounts of foreign matter. *Ground* and *sifted sulphur* for agricultural purposes should have a fineness superior to 50 degrees on Chancel's sulphurimeter.

. *Washed flowers of sulphur* and *Milk* (*Magister*) *of sulphur*, for pharmaceutical uses, should, according to the official Italian Pharmacopœia, be free from arsenic and other impurities, and should leave not more than 1% (flowers) or an inappreciable amount (milk) of residue when burnt.

*Iron pyrites* mostly contain 40–50% of sulphur.

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## CHAPTER III

# FERTILISERS

Fertilisers include many substances of organic or mineral origin, their active constituents being :

*Nitrogen*, in the form of *organic* or *insoluble nitrogen*, as it occurs in dried blood, meat guano, wool waste, horns, nails, leather, etc., bone meal, dung, guano, excrements, etc. *Nitric nitrogen*, occurring mostly in sodium and potassium nitrates. *Ammoniacal nitrogen*, in ammonium sulphate.

*Potash*, given especially by potassium nitrate, sulphate and chloride, kainit, carnallite, etc.

*Phosphoric acid*, which may occur in the insoluble state (tricalcic phosphate), as in natural phosphates (phosphorites, apatites and coprolites), bone ash, degelatinised bones, bone black, guano and other animal fertilisers ; in a condition soluble in ammonium citrate (dicalcium phosphate), as in precipitated phosphates and dephosphorisation slags ; in a condition soluble in water (monocalcium phosphate), as in the superphosphates.

Analysis of fertilisers in general comprises essentially determinations of the moisture, nitrogen, phosphoric acid (in its various forms) and potash. These determinations are described among the general methods of analysis (*see* p. 118). Other determinations to be made with special fertilisers are given in the separate cases.

Of special importance in these analyses is the taking of the samples and their preparation in the laboratory, the procedure to be followed being as described below.

**1. Taking and Despatch of Samples.**—With *homogeneous powdered fertilisers* (phosphates, bone ash, sodium nitrate, ammonium sulphate, potash fertilisers), several samples of 200–300 grams are taken either from various points and different heights of the mass if this is in heaps, or from different sacks. From these samples, which are more or less numerous according to the magnitude of the parcel, a single heap (about 3–5 kilos) is made. This is thoroughly mixed and any lumps broken to make it homogeneous, the sample for analysis being then taken.

If the fertiliser is *mixed*, that is, prepared from powdered products mixed according to definite formulæ, a larger number of samples are taken and mixed, portions from different parts of this being thoroughly mixed and the sample for analysis taken from this heap.

With *pasty fertilisers*, a number of shovelfuls are taken and mixed well, all lumps being broken down ; the sample for analysis is then taken.

With *non-homogeneous and non-pulverulent fertilisers* (bones, dried meat

and blood, nails, hair, horns and the like), a number of handfuls are taken from different parts of the mass and mixed as well as possible before the sample is taken.

*Liquid fertilisers* or *liquids with suspended or deposited matter* are well mixed with a stick.

The samples for analysis should be in three lots of at least 300 grams each for powdered fertilisers or 1 kilo in other cases.

Powdered or pasty samples are placed in glass vessels with ground stoppers or tight corks, non-pulverulent samples in new bags or wooden boxes and liquids in well cleaned bottles with new stoppers.

Each sample, duly sealed with sealing-wax, should bear a label indicating the quality of the product, the quantity from which it was taken, the origin and the date of sampling ; to this should be added a declaration of the sender indicating the nature of the material sent or that for which it has been sold, the strength (% of phosphoric anhydride, nitrogen, potash) guaranteed, and the determinations required.

**2. Preparation of the Sample in the Laboratory.**—Before analysis, the whole of the sample should be re-mixed and powdered to render it homogeneous. If, however, the degree of fineness is to be determined, the sample is mixed with a spatula and the portion necessary for such test set aside, the rest being ground in a mortar.

If the fertiliser contains hard lumps or pieces mixed with powder, it is sieved through a 0·5–1 mm. sieve, the part remaining in the sieve being powdered and re-sieved so as to obtain a uniform powder, which is finally thoroughly mixed.

Bones in lumps are broken in a mill or mortar and, if possible, powdered ; if not they are first dried at a low temperature (allowance being made for the moisture lost).

Waste wool, hair, leather, and the like are finely cut with scissors and then mixed. Horns and nails may be powdered in an ordinary mill.

Stable manure and very wet or pasty fertilisers are dried at a low temperature and then mixed and powdered, account being taken of the moisture lost (*see* General Methods, 2, and Stable Manure).

## GENERAL METHODS

These methods treat of certain preliminary tests and determinations generally applicable, except where indicated, to the different types of fertilisers.

### 1. Preliminary Tests

When the nature of a fertiliser is not definitely known, the following tests are made in order to regulate the subsequent determinations :

**1. Reaction.**—5 grams are mixed with 4–5 c.c. of water, and the reaction of the liquid tested with litmus paper.

**2. Nitrogen.**

(a) *Ammoniacal Nitrogen.* About 1 gram of the fertiliser is boiled with 5 c.c. of water and about 0·25 gram of calcined magnesia : evolution of *ammonia* indicates the presence of ammoniacal nitrogen.

(b) *Nitric Nitrogen.* 1 gram of the fertiliser is treated with 2 c.c. of water, the liquid filtered and the filtrate tested with conc. sulphuric acid and ferrous sulphate in the usual way.

(c) *Organic Nitrogen.* In absence of ammonia, 0·5 gram of the fertiliser is heated with soda lime : evolution of ammonia indicates organic nitrogen. If ammoniacal salts are present, these must be removed by extraction with water and then dried, the insoluble residue being tested with soda lime.

**3. Phosphoric Acid.**

(a) *Phosphoric Acid soluble in Water.* Half a gram is mixed with 4–5 c.c. of water and left to stand, a little of the clear liquid being pipetted off subsequently and tested with ammonium molybdate.

(b) *Soluble in Ammonium Citrate (Retrograde or reverted phosphate).* A few grams are extracted several times with water and the residual insoluble matter digested with about 20 c.c. of ammonium citrate solution (for its preparation, *see* p. 123) ; the liquid is filtered and the filtrate tested with magnesia mixture.

(c) *Insoluble.* The residue insoluble in ammonium citrate is washed several times with ammonium citrate solution boiled with 7–8 c.c. of nitric acid and allowed to stand, a little of the clear liquid being subsequently tested with ammonium molybdate.

**4. Potash.**

(a) *Soluble in Water.* About 2 grams are boiled with 10 c.c. of water and the liquid filtered.

To one portion of the filtrate an equal volume of 10% sodium thiosulphate solution is added and then 3–4 drops of *Carnot's reagent* [1] and double the volume of 95% alcohol : in presence of potash a yellow crystalline precipitate is formed.

The other portion is rendered faintly alkaline with sodium hydroxide, filtered and acidified slightly with hydrochloric acid. Addition of 1 c.c. of perchloric acid (D = 1·12) and an equal volume of alcohol yields a white precipitate in presence of potash.

(b) *Insoluble in Water.* Two grams are thoroughly exhausted with hot water and the undissolved part boiled with a mixture of 5 c.c. of conc. nitric acid and 10 c.c. of conc. hydrochloric acid, the liquid being diluted, filtered, evaporated to dryness and the residue redissolved in water ; this solution is then tested as in the preceding case.

## 2. Determination of the Moisture

From 5 to 10 grams are heated at 100° to constant weight. Superphosphates and other products rich in gypsum are dried in a boiling water-oven for 4 hours.

If the fertiliser has an alkaline reaction or it is feared that ammonia may be lost during the drying, as, for instance, with stable manure, the fertiliser (5 grams) is placed in a tared porcelain boat and this introduced into a glass tube arranged in a suitable oven. One end of the tube is con-

[1] 100 grams of basic bismuth nitrate (magister of bismuth) are dissolved in the hot in conc. hydrochloric acid and diluted to a litre with 92% alcohol.

nected with a wash-bottle containing conc. sulphuric acid and the other with a bulb-tube charged with 20 or 25 c.c. N/10-sulphuric acid. The oven is heated at 100° and during the drying a slow current of air is passed through the glass tube. The boat is finally reweighed and the loss of weight diminished by the weight of ammonium carbonate corresponding with the ammonia absorbed by N/10-sulphuric acid.

If the fertiliser has an acid reaction and it is feared that loss of volatile acid or changes rendering the estimation inaccurate will occur in drying, the fertiliser is first neutralised. To this end 5 grams are weighed in a weighing bottle, tared together with a thin glass rod. The mass is then moistened and neutralised with N-caustic soda solution. That neutralisation is approaching is indicated by the ready clarification of the supernatant liquid and the exact point determined by touching litmus paper with the rod. The liquid is then evaporated to dryness and the crust broken with the rod, drying being then continued for a further period of 4 hours. Each c.c. of N-caustic soda added increases the weight of the dry matter by 0·022 gram.

### 3. Determination of the Nitrogen

The nitrogen is determined in different ways according to its condition.

*A.* **Ammoniacal Nitrogen.**—5–10 grams of the substance are mixed with water (acidified in the case of an alkaline reaction) in a mortar, the liquid being decanted into a 250 c.c. or 500 c.c. flask. The insoluble matter is washed by decantation and the total liquid made up to volume and the ammonia in an aliquot part found by distillation with excess of sodium hydroxide (or calcined magnesia, in case organic nitrogen readily decomposable by alkali is present). The apparatus and procedure are described under Kjeldahl method (*see* later, *C*).

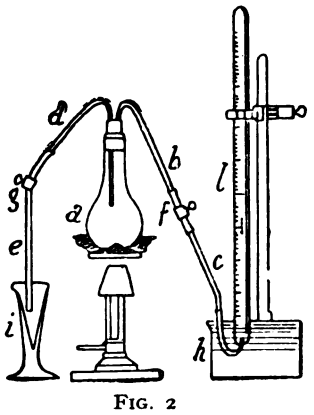

FIG. 2

*B.* **Nitric Nitrogen.** This may be determined by the two following methods:

1. SCHULZE AND TIEMANN'S METHOD. To a flask *a* of 150–200 c.c. capacity (*see* Fig. 2) is fitted a doubly-bored stopper traversed by two capillary tubes, one of which serves for the delivery of the nitric oxide into the graduated tube *l* standing over water, while the other, slightly constricted at the end, dips into a conical beaker *i*; in each tube is inserted a piece of pressure rubber tubing 5 cm. long fitted with a screw clip, *f*, *g*.

The flask is charged with 20 c.c. of 1·65 % pure sodium nitrate solution (or 20 c.c. of 2·0% potassium nitrate solution) when the fertiliser contains sodium (or potassium) nitrate, and about 30 c.c. of water. The stopper is inserted and, the two clips being open, the liquid boiled to expel all air from the flask and the capillary tubes. When the liquid is reduced to a small volume (about 15 c.c.), the delivery tube for the nitric oxide is dipped into a boiled 10% caustic soda solution and the clip closed. If the air has

been completely removed, the soda solution will fill the part of the tube below the clip immediately and completely. Shortly after, when a little water has condensed in the conical beaker so as to cover the extremity of the other capillary tube, the second clip is shut and the flame at once removed from beneath the flask.

About 15–20 c.c. of ferrous chloride solution are [1] poured into the beaker and allowed to pass into the flask by opening the clip. When the ferrous solution only just covers the tip of the capillary tube, a little hydrochloric acid (D 1·1) is poured into the beaker and later a little more, so as to wash out the beaker and displace all the ferrous chloride from the tube, care being taken that no air enters the tube and hence the flask *a* ; about 10 c.c. of acid is sufficient for this purpose. The clip is closed, the flame replaced under the flask and a graduated tube (100 c.c. reading to 0·5 c.c.) filled with boiled 10% caustic soda solution placed over the end of the gas delivery tube. When the rubber joint of this tube begins to swell, the clip is replaced by the fingers, and as soon as evolution of nitric oxide begins, the joint is left free. The boiling is regulated so that liberation of gas is not too rapid, and when this ceases the graduated tube is closed by the thumb and shaken and then placed in a bath of water.

The flask is then rinsed out and the operation repeated in identical manner with the solution of the substance to be tested. With sodium (or potassium) nitrate or fertiliser containing it, 16·5 (or 20) grams are dissolved in hot water and, if insoluble residue remains, filtered and the residue washed ; the volume is then made up to 1 litre.[2] Of this solution 20 c.c. are introduced into flask *a* if the nitrate alone is being tested or double or three times, etc., as much in the case of mixed fertilisers, so that the volume of NO collected is about the same as in the control experiment with the pure nitrate.

The second tube containing nitric oxide is placed in the same bath of water as the first and when the temperature of the gas is in equilibrium with that of the surrounding air (about 1 hour is sufficient), the two tubes are immersed in the bath so that the levels inside and outside are the same. The volume of the gas is then read off in each case at the lower edge of the meniscus.

When equal quantities of the fertiliser and pure nitrate are used, the percentage ($x$) of nitrogen is given by the formula

$$x = \frac{K(a \times 100)}{b},$$

where $K$ = the coefficient for reducing the nitrate to nitrogen and has the value 0·1647 for $NaNO_3$ and 0·1387 for $KNO_3$,

$a$ = c.c. of NO obtained from the fertiliser.

$b$ = c.c. of NO obtained from the pure nitrate.

[1] This solution is prepared by placing 200 grams of fine iron filings in a flask with 100 c.c. of water, and gradually heating the flask on a sand-bath and adding hydrochloric acid (D 1·1) until all the iron is dissolved. The liquid is filtered to get rid of carbon and made up to 1 litre with boiled water.

[2] If the fertiliser contains carbonate, the solution is prepared with water containing hydrochloric acid to eliminate the carbon dioxide. If the fertiliser contains oxalic acid (guano), the latter is rendered insoluble by addition of a little milk of lime.

The percentage ($x$) of $NaNO_3$ or $KNO_3$ may be calculated by the formula,

$$x = \frac{a \times 100}{b}.$$

2. JODLBAUR'S MODIFIED KJELDAHL METHOD. This is applied in the manner indicated under *D* for the total nitrogen. With nitrates 0·5 gram is taken, and with mixed fertilisers 1 gram. $N \times 0{\cdot}1647 = NaNO_3$; $N \times 0{\cdot}1387 = KNO_3$.

The result obtained by this method must, of course, be diminished by the porportions of ammoniacal and organic nitrogen (found under *A* and *C*) present.

*C*. **Organic Nitrogen.**—This is determined by *Ulsch's* modification of the *Kjeldahl method*:

Into a long-necked, pear-shaped flask of good resistant glass holding about 250 c.c.[1] from 1 to 5 grams (according to the nitrogen content) of the substance are introduced,[2] together with 20–25 c.c. of *phosphosulphuric acid* (125 grams of phosphoric anhydride dissolved in 1 litre of sulphuric acid of 66° Baumé), 2–3 drops of 10% platinum chloride solution, and 0·2–0·3 gram of copper oxide.

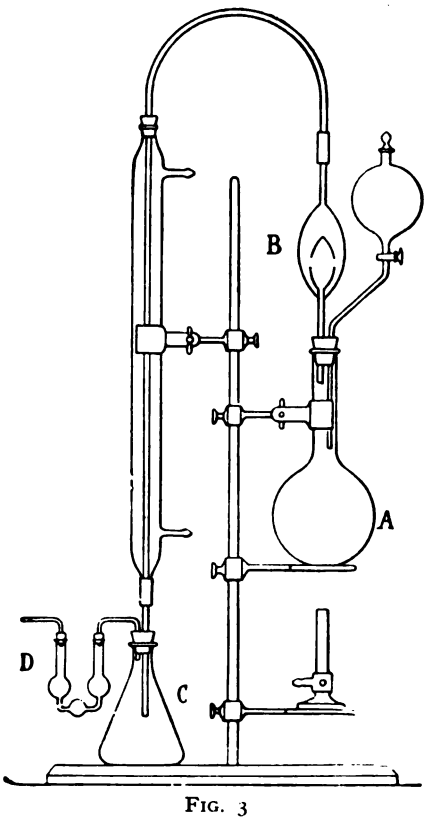

FIG. 3

The flask is closed with a small funnel or, better, with a light glass bulb drawn out to a point at one end, and is then placed sloping on an asbestos-covered gauze and heated, at first with a small flame and then to boiling until a clear and almost, if not quite, colourless solution is obtained. In this way the organic nitrogen is wholly converted into ammonium sulphate.

When cold, the liquid is carefully diluted with water and washed out into a flask of about 1 litre capacity. The liquid is then rendered alkaline with excess of sodium hydroxide solution (about 30%) and the ammonia distilled, an apparatus similar to that shown in Fig. 3 being used. The flask *A* contains the alkaline liquid to be distilled, the bulb *B* serves to retain any alkali spurting over and is formed of two concentric glass bulbs, the

[1] Suitable flasks and other accessories for the Kjeldahl method are sold.

[2] With liquids, such volume or weight is taken as corresponds with 1–5 grams of solid substance, according to the nitrogen content. The liquid is then evaporated to dryness in the Kjeldahl flask itself.

inner one with two lateral orifices ; the conical flask *C* contains 20–25 c.c. (exact amount) of N/2-sulphuric acid and the safety tube *D* a little water.

When 200–250 c.c. of liquid have distilled over, the flask *C* and tube *D* are detached, the latter being washed into the flask and the contents of the latter titrated with N/2-sodium hydroxide in presence of methyl orange. The number of c.c. of N/2-acid neutralised, multiplied by 0·007, gives the amount of nitrogen in grams in the weight of substance taken for analysis. In cases where ammoniacal nitrogen is present as well as organic nitrogen, the result just obtained must be diminished by that obtained by method (*A*).

*D.* **Total Nitrogen.**—The preceding methods give the total nitrogen where this is all of one form or a mixture of ammoniacal and organic. If, besides these two, nitric nitrogen is also present, the total nitrogen is determined as follows :

Jodlbaur's modification of the Kjeldahl method. From 1 to 5 grams of substance [1] are well mixed in a Kjeldahl flask with 20 c.c. of *phenol-sulphuric acid* solution (40 grams of phenol dissolved in 1 litre of sulphuric acid of 66° Baumé) and, after 5 minutes, 2–3 grams of zinc dust are added in small portions and with cooling. The flask is then heated over a small flame for 10–15 minutes, allowed to cool and 5 c.c. of phosphosulphuric acid (*see* under *C*), a little copper oxide and a few drops of platinic chloride solution added, the subsequent procedure being as in the Ulsch method (*see* under *C*).

The official Italian methods conform to those given above, but they allow also : (1) for nitric nitrogen, of the use of Ulsch's method, which consists in reduction of nitrates to ammonia by means of reduced iron or zinc, and of Devarda's method, in which the reduction is effected by aluminium or zinc in alkaline solution ; (2) for the total nitrogen of the use of Dumas' method.

## 4. Determination of the Phosphoric Acid

Determinations may be required of the total phosphoric acid, of that soluble in water, and of that soluble in ammonium citrate. Here is described only the method for the total phosphoric acid, applicable to all phosphatic fertilisers except Thomas slag (*q.v.*). Estimation of the phosphoric acid soluble in water or in citrate, applicable essentially to superphosphates and other slags, is treated later in dealing with these products in particular.

**Determination of the Total Phosphoric Acid.**—The following solutions are required :

(a) *Ammonium citrate.* 400 grams of crystallised citric acid are covered with water and neutralised with ammonia (D = 0·92) (about 500 c.c. required), the liquid being cooled meanwhile and finally made up to 1 litre.

(b) *Magnesia Mixture.* 110 grams of crystallised magnesium chloride, 140 grams of ammonium chloride, 700 c.c. of 8% ammonia (D = 0·967) and 1300 c.c. of water.

(c) *Ammonia,* D = 0·920.

PROCEDURE. Five grams of the substance are boiled for about 30 minutes in a 250 c.c. measuring flask with 50–75 c.c. of water, 20 c.c. of

[1] If this is moist or difficult to attack, it is well to add 2–3 grams of finely powdered burnt gypsum.

hydrochloric acid and 5 c.c. of conc. nitric acid, and subsequently diluted with water, allowed to cool, made up to volume and filtered.

To 25 c.c. of the filtrate (= 0·5 gram of substance), or 50 c.c. (= 1 gram) with a poor phosphate, are added 20 c.c. of the ammonium citrate, 50 c.c. of water, 50 c.c. of ammonia (D 0·92) and 50 c.c. of magnesia mixture, the whole being then stirred vigorously without the stirrer touching the walls of the vessel. After being stirred continuously for 30 minutes with a mechanical stirrer or, if this is not available, after standing for at least 5–6 hours, the liquid is filtered and the precipitate washed, first by decantation and then on the filter with ammonia (1 vol. of ammonia of D = 0·96 and 3 vols. of water) until the wash liquor is free from chloride. The filter is then dried at 100°, the precipitate detached, the filter-paper burnt separately and precipitate and filter-ash heated together in a platinum crucible until of constant weight. The weight of magnesium pyrophosphate thus obtained, multiplied by 128 when 0·5 gram of substance was taken or by 64 for 1 gram, gives directly the amount of phosphoric anhydride ($P_2O_5$) per 100 grams of substance, the results being always expressed in this form.

Menozzi's modification (1898) of Pemberton's volumetric method is also included among the Italian official methods.

## 5. Determination of the Potash

From 5 to 10 grams of substance [1] are heated to boiling with 200–250 c.c. of water and 5–10 c.c. of conc. hydrochloric acid in a 500 c.c. measuring flask. When cool, the liquid is made up to volume and mixed, 100 c.c. of the solution (1–2 grams of substance) being then transferred to another 500 c.c. flask and boiled. At this point, if the material is rich in sulphate, barium chloride solution is added until no further precipitation occurs and then slight excess of baryta water (phenolphthalein being added to the liquid, the baryta is added until the solution turns red) ; if the material is poor in, or free from, sulphate, baryta solution alone is added. When cold, the liquid is made up to volume, shaken, and filtered through a dry filter, 250 c.c. of the filtrate (0·5–1 gram of substance) being introduced into another 500 c.c. flask and boiled. Ammonium carbonate solution is then gradually added, with constant agitation, as long as precipitate is formed, the flask being heated for some time on a steam-bath in order that the precipitated barium carbonate may become crystalline. When cold, the volume is made up and the liquid shaken and filtered.[2]

[1] With complex organic fertilisers, 10–20 grams (according to the supposed richness in potash) are charred in a platinum dish at a red heat, the mass being extracted with water and conc. hydrochloric acid and the liquid evaporated to dryness. The residue is heated at 120°, dissolved in dilute hydrochloric acid, transferred to a 500 c.c. flask, made up to volume and mixed. An aliquot part of the liquid is then treated with barium chloride, baryta, etc., in the ordinary way.

[2] With potassium chloride or sulphate, the treatment with barium chloride, baryta water and ammonium carbonate may be made successively in the original flask in which the substance (5 grams) is dissolved, the volume being then made up and the liquid shaken and filtered, 25 c.c. of the filtrate (= 0·25 gram of substance) being then taken. At this dilution the volume occupied by the precipitate is without appreciable influence.

Of the filtrate, 250 c.c. are evaporated to dryness, gently ignited to expel the ammonium salts, the residue being dissolved in hot water and the solution filtered through a small filter, which is well washed with hot water. The liquid is evaporated to a small volume (about 10 c.c.) in a porcelain or glass dish on a steam-bath and the potassium determined by one of the following methods:

(*a*) PLATINUM CHLORIDE METHOD. The small quantity of liquid is evaporated to a syrup with 25 c.c. of 10% platinum chloride solution, being frequently stirred with a glass rod; 50 c.c. of alcohol (85·5% by volume = 80% by weight) are then stirred in and after an hour the liquid filtered through a filter dried at 100° and tared, the precipitate being well washed with alcohol of the above strength, dried at 100° and weighed.[1] $K_2PtCl_6 \times 0{\cdot}194 = K_2O$.

(*b*) PERCHLORATE METHOD. The concentrated solution, in a glass dish, is evaporated on a water-bath with about 15 c.c. of perchloric acid of D 1·12 (about 20%) until the hydrochloric acid is completely expelled and white fumes of perchloric acid appear. On cooling, the residue is mixed with 25 c.c. of approximately 95% alcohol containing 0·2% of perchloric acid, all lumps being broken up with a glass rod. After the lapse of 30 minutes, the precipitate is collected on a Gooch crucible previously dried at 120° and weighed, washed with not more than 70–75 c.c. of 95% alcohol containing 0·2% of perchloric acid and finally with pure 95% alcohol. It is then dried at 120° and weighed. The content of potash is expressed as percentage of $K_2O$.

## SPECIAL PART

# Nitrogenous Fertilisers

## AMMONIUM SULPHATE

A crystalline powder, greyish or sometimes reddish, yellowish or bluish according to the impurities it contains; the pure salt is colourless.

The determinations and tests to be made are as follows:

**1. Moisture.**—5 grams are heated at 110–120° to constant weight.

**2. Nitrogen.**—10 grams are dissolved in water to 1 litre and 50 c.c. of this solution (= 0·5 gram of substance) distilled with sodium hydroxide (*see* General Methods, 3, *A*).

**3. Fixed Residue.**—3 grams are ignited until no further evolution of volatile matters takes place.

**4. Thiocyanates.**—2 grams are dissolved in 20 c.c. of water and a little hydrochloric acid and ferric chloride added: in presence of thiocyanates a red coloration forms.

[1] Instead of a filter-paper a Gooch crucible may be used. The precipitate is collected in this, dried at 100° and weighed. The crucible is then washed with boiling water to dissolve the precipitate, again dried and weighed. The loss in weight gives the potassium platinichloride.

**5. Free Sulphuric Acid.**—A solution of 20 grams in water is titrated with N/2-sodium hydroxide in presence of methyl orange.

* * *

Pure ammonium sulphate contains 21·21% N and should leave no residue on ignition. The commercial salt should contain at least 19% N, but usually contains 20–21%.

## SODIUM NITRATE (Chili Saltpetre)

Minute grey or yellowish crystals containing, as impurities, chlorides, sulphates, insoluble substances and perchlorates. The more important tests and determinations are as follows:

**1. Moisture.**—5 grams are heated in an oven at 110–120° to constant weight. The nitrate may also be weighed in a crucible, heated carefully to incipient fusion, allowed to cool in a desiccator and re-weighed.

**2. Various Impurities.**—The insoluble matter, chlorides, sulphates, lime, etc., are detected and, where necessary, estimated by the ordinary analytical methods.

**3. Detection of Perchlorates.**—10–20 grams are dissolved in as much water and filtered, a few drops of the filtrate being treated on a microscope slide with 1–2 crystals of rubidium chloride and the liquid coloured pink with one or two drops of dilute potassium permanganate solution. After careful evaporation over a very small flame until a crust forms at the edges of the liquid, a cover-slip is placed on the drop and the latter examined under the microscope: the presence of perchlorate is indicated by dark violet-red, rhombic crystals of rubidium perchlorate, often in stellate groupings, by the side of the colourless sodium nitrate crystals.

**4. Determination of Perchlorate.**—This may be carried out as follows:

The chlorine in the nitrate is first determined by one of the ordinary methods. Another portion of 5 or 10 grams of the finely powdered nitrate is mixed with pure calcium oxide (8 grams) or carbonate (15 grams) (quite free from chlorine) and the mixture heated for about 15 minutes in a platinum or porcelain crucible. The mass is then dissolved in dilute nitric acid and the chlorine again determined. The increase in the percentage of chlorine, multiplied by 3·4556, gives the percentage of $NaClO_4$.

If, besides perchlorate, the nitre contains also chlorate, the latter is calculated as perchlorate.

**5. Nitrogen.**—*See* General Methods, 3, *B*.

**6. Determination of the Sodium Nitrate.**—The amount of $NaNO_3$ may be calculated by multiplying the percentage of nitrogen by 6·0714. Usually, however, and especially with nitre for industrial purposes, the nitrate is determined either by decomposing it with sulphuric acid in presence of mercury and measuring the volume of nitric oxide formed, or by difference after the extraneous substances have been estimated. The methods to be applied in the two cases are as follows:

1. NITROMETRIC METHOD (*Lunge*). This makes use of the *Nitrometer, shown in Fig. 4,* and consisting of two glass tubes, *A* and *B*, the former

graduated, connected by rubber tubing. Mercury is poured into *B* and forced into *A* by opening the tap *r* and raising *B* ; in this way *A* is filled with mercury (care being taken that no air bubbles remain along the walls of the tube) to the tap, which is then closed.

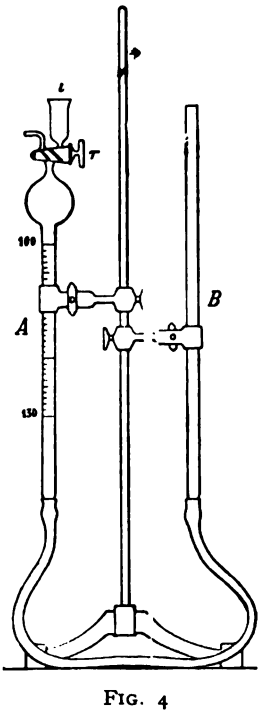

FIG. 4

From 0·35 to 0·45 gram of the finely powdered nitrate (which gives not less than 100 and not more that 130 c.c. of NO) are placed in the funnel *i* in which it is shaken with about 0·5 c.c. of hot water until dissolved. Tube *B* is then lowered and the tap *r* carefully opened, so that the solution, but no air, enters *A*. The funnel is washed with not more than 1 c.c. of hot water, which is also cautiously introduced into *A*. Finally about 15 c.c. of pure conc. sulphuric acid are run into *A*, which is shaken vigorously to induce the reaction between nitrate, sulphuric acid and mercury, by which the whole of the nitrogen of the nitrate is converted into nitric oxide. After the lapse of at least half an hour, the tube *B* is raised until the mercury is at the same level in *A* and *B*, the volume of the gas being read, and also the temperature and barometric pressure.

The volume of the gas ($V$) at 0° and 760 mm. is given by the formula, $V = \frac{vp}{760(1 + 0{\cdot}00367\,t)}$, where $v$ is the volume of the gas in the nitrometer, $p$ the atmospheric pressure and $t$ the temperature. The amount of $NaNO_3$ in the quantity of nitrate taken is equal to 0·0038 times $V$.

2. INDIRECT METHOD. The moisture, insoluble matter, chlorine and sulphuric acid are determined by the ordinary methods, the last two constituents being calculated as NaCl and $Na_2SO_4$. The sum of the percentage of these four ingredients is then subtracted from 100, the remainder being the percentage of $NaNO_3$.

***

Pure sodium nitrate contains 16·5% of nitrogen, while the commercial products for fertilising purposes generally contain about 15%. The mean composition of the Chili saltpetre coming to Europe is :

| | |
|---|---|
| Sodium nitrate | 94–96% |
| Sodium chloride | about 1% |
| Sodium sulphate | ,, 0·5% |
| Insoluble matter | ,, 0·2% |
| Moisture | ,, 2% |

Among the impurities of importance in sodium nitrate is perchlorate (harmful), which may be present in proportions varying from 0·3 to 5·6%, but is usually about 1% ; the percentage of chlorate varies from 0·1 to 1. Commercial sodium nitrate may be adulterated with salts almost devoid of fertilising value, such as sodium sulphate, and samples containing 20–40% and even 60% of this salt have been met with.

### Other Nitrates

*Potassium* and *Calcium nitrates* are also used in agriculture. In the former the nitrogen is estimated as in sodium nitrate and the other tests indicated in the article on potassium nitrate (chapter on "Chemical Products"), and the determination of the potassium may also be carried out (*see* General Methods, 5). With calcium nitrate the determination of the nitrogen is usually sufficient.

The calcium nitrate (obtained from synthetic nitric acid) now sold as a fertiliser is of various kinds: *neutral*, with about 13% N; *basic*, with 10% N; and *nitrato-nitrite*, with 14·5% N.

## CALCIUM CYANAMIDE

The commercial product is a greyish-black, fine or granulated powder and consists of a mixture of calcium cyanamide ($CaCN_2$) with lime, carbon and various impurities (calcium carbide, sulphur and phosphorus compounds, silica, etc.).

Its value depends essentially on its nitrogen content, which is determined by Ulsch's modified Kjeldahl method (*see* General Methods, 3, *C*) on 0·5–1 gram of substance. The action is to be regarded as complete after about three hours' boiling with phosphosulphuric acid, since the liquid does not become clear and colourless owing to the presence of carbon in suspension. It is also sufficient to boil 1 gram of the substance for 2 hours with 30 c.c. of dilute sulphuric acid (1 : 1) and a drop of mercury.

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Pure calcium cyanamide ($CaCN_2$) contains 33% N; the commercial product, consisting on the average of 60% of the cyanamide, 20% of lime, 10% of carbon and 10% of various extraneous substances, contains 15–22% N.

# Phosphatic Fertilisers

## PHOSPHATES

By phosphates are understood products containing tricalcium phosphate, $Ca_3(PO_4)_2$, such as *Mineral phosphates* (*phosphorites, apatites, coprolites*); *bones*, such as *bone meal* and *bone ash*; and *bone black*.

Analysis of these products includes mainly determinations of the moisture and phosphoric anhydride; in some cases also the nitrogen (in bones and the ash of raw bones), ferric oxide and alumina (in mineral phosphates) and others indicated in 5 (below), when a complete analysis is required.

1. **Moisture.**—*See* General Methods, 2.

2. **Phosphoric Anhydride** (total).—*See* General Methods, 4.

3. **Nitrogen.**—*See* General Methods, 3, *C*.

4. **Ferric Oxide and Alumina.**—*Glaser's method.* 5 grams of the substance are boiled for about 30 minutes in a 250 c.c. measuring flask with 50–75 c.c. of water, 20 c.c. of conc. hydrochloric acid and 5 c.c. of conc. nitric acid, the liquid being made up to volume on cooling and filtered.

50 c.c. of the filtrate (= 1 gram of substance) are shaken in another 250 c.c. flask with 50 c.c. of water and 25 c.c. of conc. sulphuric acid, allowed to stand for about 15 minutes and then well shaken with 100 c.c. of 95–96% alcohol. When quite cold, the liquid is made up to volume with alcohol, mixed and again made up to volume (contraction occurring); after mixing, the solution is left for at least 30 minutes and filtered. 100 c.c. of the filtrate (= 0·4 gram of substance) are evaporated almost to dryness in a porcelain dish and the residue taken up in water,[1] heated on a water-bath and treated with a slight excess of ammonia, which precipitates the iron and aluminium as phosphates. The heating is continued until the excess of ammonia is expelled, the liquid being filtered when cold and the precipitate washed with hot water, dried, ignited and weighed. The weight, divided by 2, gives $Fe_2O_3 + Al_2O_3$ in 0·4 gram of substance.

**5. Other Determinations.**—For complete analysis, which is required more especially with mineral phosphates, the determinations indicated briefly below[2] are necessary in addition to those given above:

*Fluorine*, by transformation into silicon fluoride by treatment with silicious sand and sulphuric acid, the fluoride being subsequently decomposed by water and the hydrofluosilicic acid formed titrated (Penfield's or Offermann's method).

*Chlorine*, by dissolving the phosphate in nitric acid and estimating the chlorine volumetrically by the usual methods.

*Sulphuric acid*, by precipitation as barium sulphate from the hydrochloric acid solution of the phosphate.

*Carbon dioxide*, by treatment of the phosphate with an acid and absorption of the carbon dioxide by potassium hydroxide in the usual manner.

*Silica*, by treatment of the substance with aqua regia so as to render the silica insoluble.

*Manganese*, by dissolving the substance in aqua regia, eliminating the iron, phosphates, etc., by means of zinc oxide and titration of the manganous salt, remaining in solution, with permanganate.

*Lime*, by weighing the calcium sulphate remaining undissolved in alcohol in the determination of the oxides of iron and alumina by Glaser's method (*see* 4), or by dissolving the substance in hydrochloric acid, precipitating with ammonia, redissolving in acetic acid and separating the lime as oxalate.

*Magnesia*, by precipitation as magnesium ammonium phosphate after elimination of the lime.

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*Mineral phosphates* may contain (%): moisture, 0·3–8; $P_2O_5$, 10–55; CaO, 22–57; $Al_2O_3 + Fe_2O_3$, 0·2–10; $CO_2$, 2–24; $SiO_2$, 2–8. Small amounts of fluorine (more than 0·1% $CaF_2$) and manganese are almost always present.

*Bones* and *bone ash* may contain 37–40% $P_2O_5$, and up to about 4% N.

*Bone black* (refinery waste, etc.) usually contains 20–40% of water and 25–30% $P_2O_5$.

[1] If the phosphate contains organic substances, it is well at this point to take up with hydrochloric acid and a few drops of bromine, to boil until bromine vapours disappear, to dilute with water, and to precipitate with ammonia as above.

[2] The detailed methods may be found in special works dealing with the analysis of fertilisers or, more particularly, of phosphates.

## SUPERPHOSPHATES

In these products the phosphoric acid occurs mostly as monocalcium phosphate, $Ca(H_2PO_4)_2$, and to a less extent as dicalcium phosphate, $CaHPO_4$, that is, in two forms soluble in water and in ammonium citrate ; smaller quantities may occur as tricalcium phosphate, insoluble in water or the citrate, but soluble in acids. Superphosphates contain also free phosphoric and sulphuric acids, calcium sulphate, silica and other extraneous substances, according to their origin (*see* later).

Superphosphates are distinguished as *bone superphosphates* ; *mineral superphosphates* ; and *double*, *triple* and *enriched superphosphates*, which are obtained by treating the phosphates with phosphoric acid.

The analysis of these products includes the following :

**1. Moisture.**—*See* General Methods, 2.

**2. Phosphoric Anhydride.**—That soluble in water and ammonium citrate, and that soluble in water alone, are determined.

*A*. PHOSPHORIC ANHYDRIDE SOLUBLE IN WATER AND IN AMMONIUM CITRATE (*Appiani's method*). This requires the solutions (ammonium citrate, magnesia mixture and ammonia) prescribed for the determination of the total phosphoric acid (*see* General Methods, 4) : 5 grams of the superphosphate (2·5 grams with double or triple superphosphate) are made into a paste in a mortar with 40–50 c.c. of water, allowed to stand a few minutes and the liquid decanted on to a pleated filter, the filtrate being collected in a 250 c.c. measuring flask. This treatment with water is repeated three or four times, the operations being regulated so that the digestion lasts only a few minutes and the filter is always empty when the decanted liquid is placed in it. The whole of the solid matter is finally washed on to the filter and there washed until the volume of the total filtrate occupies nearly 250 c.c. ; a few drops of hydrochloric or nitric acid are then added and the volume made up with water (*aqueous solution*).

The filter and its contents are introduced into another 250 c.c. measuring flask and digested with 100 c.c. of the ammonium citrate solution [1] for an hour at 35–40°, with frequent shaking ; when cool, the volume is made up to 250 c.c. with water and the liquid shaken and filtered (*citric solution*).

To 50 c.c. of the aqueous solution are added 50 c.c. of the citric solution, 50 c.c. of water, 50 c.c. of ammonia (D 0·92) and then, gradually and with shaking, 50 c.c. of magnesia mixture. After the whole has been well shaken,

[1] This amount of citrate is usually more than sufficient to dissolve all the dicalcium phosphate in the residue insoluble in water from ordinary commercial superphosphates, in which form four-fifths to nine-tenths of the phosphoric acid soluble in citrate is soluble in water. With precipitated phosphates, with superphosphates of high grade but poor in phosphoric acid soluble in water, and with phosphates quite free from monocalcium phosphate, so that part of the phosphate might remain undissolved, it is advisable to use more citrate or to work with a smaller quantity of substance.

With double and triple superphosphates, meat guano, or excessively dry superphosphates, in order to include also any pyro- and meta-phosphoric acids present it is advisable, before precipitating the phosphoric acid, to heat the solution for some time with a little nitric acid to transform into phosphoric acid the pyro- and meta-phosphoric acids which may be formed during drying.

the procedure is as indicated on p. 123 for the determination of the total phosphoric acid. $Mg_2P_2O_7 \times 0{\cdot}64 = P_2O_5$ per 1 gram of substance.

*B.* PHOSPHORIC ANHYDRIDE SOLUBLE IN WATER. To 50 c.c. of the aqueous solution prepared as in *A* are added 20 c.c. of ammonium citrate, 50 c.c. of water, 50 c.c. of ammonia (D 0·92) and 50 c.c. of magnesia mixture. This is shaken and treated exactly as in *A*.

**3. Nitrogen.**—This is determined particularly in bone superphosphate or for the detection of adulteration (*see* 5) by Ulsch's modification of the Kjeldahl method (*see* General Methods, 3, *C*).

**4. Degree of Fineness.**—25 or 50 grams of the superphosphate simply mixed with a spatula (not powdered) are sieved for 5 minutes through a sieve of 1–2 mm. mesh, the percentage passing through being determined.

**5. Adulterations.**—These should be tested for with so-called bone superphosphates, which have the greatest value and are therefore the most often adulterated. As adulterants, use is made more particularly of mineral superphosphates, bone ash, bone black ; precipitated phosphates ; pyrophosphates and superphosphates obtained from them ; gypsum, calcareous substances (chalk, powdered oyster shells) ; sand, road dirt ; various organic nitrogenous substances (dried blood, leather or wool waste, residues from the purification of illuminating gas).

The detection of adulteration in bone superphosphate is not always easy or certain. Preliminary tests to distinguish bone from mineral superphosphate and to detect certain other adulterants are as follows :

(*a*) The sample is made into a paste with water and filtered : bone superphosphate gives a clear, coloured filtrate, whereas mineral superphosphate gives a turbid, colourless one.

(*b*) The sample is heated in a porcelain dish over an ordinary flame until charred and then in a platinum dish over a blowpipe flame vigorously and for a long time. Bone superphosphates give no white fumes, but only an odour of sulphur dioxide, and a white or faintly yellow, incandescent mass, which is white or barely reddish when cold ; mineral superphosphates give white fumes of $SO_3$ and a mass which is yellow when hot and brick-red in the cold. Further, the residue from bone superphosphate is completely, or almost completely, soluble in hot 10% hydrochloric acid, whilst mineral superphosphate leaves a more or less abundant residue insoluble in the dilute acid.

(*c*) The aqueous solution of the sample is tested for chloride, a marked proportion of the latter indicating the presence of precipitated phosphate.

(*d*) Abundant effervescence when the sample is treated with hydrochloric acid indicates addition of calcareous substances.

A complete examination requires, however, systematic investigations and determinations including : microscopic observations or a petrographical study, determinations of the total and citrate-soluble phosphoric acid, sulphuric anhydride, silica, insoluble residue, nitrogen in the latter, fluorine, chlorine, lime, alumina and ferric oxide and manganese.[1]

[1] *See* E. Lasne : " Detection of Adulteration of Bone Superphosphate " (*Staz. sper. agrar. ital.*, 1898, p. 270) ; F. Martinotti : " A Method for Distinguishing Bone Phosphates from Mineral Phosphates " (*ibid.*, 1897, p. 663) ; G. Masoni : " Contribution to the Detection of Adulterants in Bone Superphosphate " (*ibid.*, 1910, p. 297).

Commercial superphosphates contain 14–20% of $P_2O_5$ soluble in water and citrate; their strength, in percentage of $P_2O_5$, is only guaranteed as 14/16, 15/17, 16/18, 18/20. The normal percentage of moisture is 10–15 in mineral superphosphates and 13–16 in those from bones.

*Bone superphosphates* contain 1–1·5% of organic nitrogen and are to be regarded as genuine when they contain less than 0·1% $Al_2O_3 + Fe_2O_3$, less than 0·1% $CaF_2$, less than 0·05% $CaCl_2$, less than 1% $SiO_2$, less than 0·3% of residue insoluble in acids, (and this is free from nitrogen) and no manganese, and when the value of the ratio CaO : $P_2O_5$ lies between 1·30 and 1·35, that of $SO_3 \times 100$ : total $P_2O_5$ is 110–129, and that of $SO_3 \times 100$ : soluble $P_2O_5 = 110$–132 (in the last two ratios $SO_3$ and $P_2O_5$ are referred to 100 parts of dry substance).

The *mineral superphosphates*, on the other hand, contain no nitrogen, but relatively large proportions of alumina and ferric oxide, fluorine, silica and insoluble residue; further the ratio $SO_3 \times 100$ : total $P_2O_5 = 181$–227 and $SO_3 \times 100$ : soluble $P_2O_5 = 184$–242 ($SO_3$ and $P_2O_5$ referred to dry substance).

*Double* and *triple superphosphates* contain 40–45% $P_2O_5$.

## SLAGS

Dephosphorisation slag, or *Thomas slag*, forms a fine, brownish-grey powder, and it contains calcium phosphate, mostly (75–70% of the total $P_2O_5$) soluble in ammonium citrate or citric acid, and on this its value depends. Analysis of this product comprises the following:

**1. Total Phosphoric Anhydride** (*Loge's method*).—5 grams of substance, placed in a 250 c.c. measuring flask, are moistened with water, 25–30 c.c. of conc. sulphuric acid added, and the flask, covered with a funnel, heated on a gauze or sand-bath until white vapours are emitted; the liquid is then diluted with water, allowed to cool, made up to volume with water and mixed. To 50 c.c. of the filtered liquid (= 1 gram of substance) are added 20 c.c. of ammonium citrate, 50 c.c. of water, 50 c.c. of ammonia (D = 0·92), and 50 c.c. of magnesia mixture, the procedure then being that for the ordinary determination of total phosphoric anhydride (*see* General Methods, 4).

**2. Phosphoric Anhydride soluble in Citric Acid** (*Wagner's method*).—The following solutions are required:

(a) *Citric Acid.* 100 grams of the crystallised acid and 0·05 gram of salicylic acid are dissolved in water to 1 litre. Immediately before use, 1 vol. of this solution is diluted with 4 vols. of water, this giving the 2% *citric acid solution* necessary for the determination.

(b) *Molybdic solution.* 150 grams of pure ammonium molybdate are dissolved in 500 c.c. of water and the solution poured into 1 litre of nitric acid (D 1·19), 400 grams of ammonium nitrate being added, the volume made up to 2 litres with water, the liquid left at about 35° for 24 hours and then filtered.

(c) *Magnesia mixture.* This is prepared as indicated on p. 123.

MODE OF WORKING:

5 grams of slag, in a graduated 500 c.c. flask, are moistened with 5 c.c. of alcohol and the volume made up, gradually and with thorough shaking, with the 2% citric acid solution. It is then rotated mechanically

at 30–40 turns per minute for half an hour at a temperature of 17·5°, and immediately afterwards filtered.

In a cylindrical beaker, 50 c.c. of the filtrate (= 0·5 gram of substance) are heated on a water-bath at 65° for 15 minutes with 80–100 c.c. of the molybdic solution (*b*). When cool, the mixture is filtered and the ammonium phosphomolybdate washed with 1% nitric acid and dissolved in about 100 c.c. of 2% ammonia ; after addition of 15 c.c. of magnesia mixture (*c*) and shaking, the procedure is as in the determination of the total phosphoric anhydride (*see* p. 123).

**3. Free Lime.**—10 grams of the slag are treated with about 250 c.c. of water in a 500 c.c. measuring flask, with frequent shaking over several hours. When the volume has been made up with water and the liquid mixed and filtered, 50 or 100 c.c. (= 1 or 2 grams of substance) are titrated with N/2-hydrochloric acid and phenolphthalein. 1 c.c. N/2-HCl = 0·014 gram CaO

**4. Degree of Fineness.**—50 grams of the slag as received are sieved for 15 minutes with a No. 100 Kahl sieve 20 cm. in diameter. The weight remaining in the sieve is subtracted from 50 grams and the remainder multiplied by 2 to give the percentage of fine slag.

**5. Specific Gravity.**—This is determined with an ordinary picnometer, alcohol or essence of turpentine being used as the liquid.

**6. Adulterations.**—Thomas slag is adulterated with mineral phosphates, aluminium phosphate or Redonda phosphate, Martin slag, Wolter and Wiborg phosphates (artificial slags) and coal dust.

For detecting natural phosphates and aluminium phosphate, recourse may be had to microscopic examination, to determinations of the specific gravity, of the loss on ignition and of the portion soluble in hot water and to tests for fluorine, carbonates and alumina (the slag is shaken in the cold with sodium hydroxide solution and the liquid filtered, acidified with hydrochloric acid and tested with ammonia).

Martin slag and Wolter and Wiborg phosphates are indistinguishable from the Thomas slag, but in general are less rich in phosphoric anhydride.

Coal dust may be observed under a lens or by shaking the slag with water (the coal floats).

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Genuine Thomas slag contains 11–23% of total $P_2O_5$ (on the average about 17%) and 9·5–16% of $P_2O_5$ soluble in citric acid (on the average, 12·5–13·5%). It contains also 41–52% of total CaO (mean, 46–47%), 3–6% MgO, 9–28% of ferroso-ferric oxide (mean, about 15), 3–8% $SiO_2$ (mean, about 7), and about 10% of matter soluble in hot water. It contains only very small quantities of alumina and no fluorine, and on calcination loses not more than 1% of its weight. Its specific gravity is 3–3·3, and under the microscope it is seen to be composed of small, yellowish, acute-angled splinters.

As regards the testing of the genuineness of *mineral phosphates*, it must be borne in mind that, unlike Thomas slag, these do not contain $P_2O_5$ soluble in citric acid, and are almost entirely insoluble in hot water ; on ignition, they lose considerably in weight (water, $CO_2$) ; they contain fluorine ; their specific gravities are below 3, and under the microscope they are seen to consist of roundish granules. *Redonda phosphate* is detected by testing for aluminium (abundant precipitate in test 6).

## PRECIPITATED PHOSPHATE

Fine, yellowish white powder, composed essentially of dicalcium phosphate, $CaHPO_4$, and hence mostly soluble in ammonium citrate.

Consequently, the citrate-soluble phosphoric anhydride is determined in these products, using the method employed with superphosphates (*see* Superphosphates, observing note 1 on p. 130).

Any adulteration with mineral phosphate, gypsum or chalk, may be detected as in superphosphates.

Precipitated calcium phosphate contains on an average 40–42% $P_2O_5$ soluble in citrate, and 2–3% $P_2O_5$ insoluble in citrate but soluble in acids, 7–8% of moisture, 2–3% of chlorine (chloride resulting from the method of preparation) and small proportions of alumina, ferric oxide and sulphates.

# Potash Fertilisers

The most important potash fertilisers consist of *Stassfurt salts*, those most used being ordinary *potassium chloride* and *sulphate*. Use is also made of *carnallite* (potassium and magnesium chlorides, with magnesium sulphate and sodium chloride); *kainit* (potassium and magnesium sulphates, with magnesium and sodium chlorides); *sylvine* (sodium and potassium chlorides, with sulphates); *hard salt* (composition similar to that of Kainit); *potash manure salts* (potassium chloride with varying proportions of magnesium sulphate and chloride, sodium chloride and calcium sulphate).

The value of these products depends naturally on their content of $K_2O$, and for agricultural purposes it is sufficient to determine this by the method given on p. 124.

Where, for special purposes, a complete analysis or at least a knowledge of the content of sodium chloride is required, the following procedure is pursued.[1]

### *A.* Complete Analysis

This includes the following determinations:

**1. Moisture.**—10 grams are heated at a dull red heat in an open platinum crucible for 10 minutes. If the salt contains magnesium chloride, it is covered with a layer of ignited quicklime.

**2. Insoluble Substances.**—100 grams of the salt are dissolved in about 400 c.c. of boiling water, the solution filtered through a tared filter, the residue being well washed and the filtrate made up to 1000 c.c. The filter is then dried and weighed.

**3. Sulphuric Acid, Chlorine, Lime, Magnesia.**—These are determined in aliquot parts of the above solution by the ordinary methods.

**4. Alkalies.**—100 c.c. of the solution prepared as in 2 (= 10 grams of substance) are introduced into a 500 c.c. flask and treated as in *B* (below).

[1] More detailed notices on the analysis of potassium salts may be found in *Analyse des engrais*, by D. Sidersky (Paris, 1901), and in a memoir by H. Roemer on "Méthodes pour l'analyse des sels de potasse," published in *Bull. de l'association des chim. de sucr., 1911–1912, Vol. 29, p. 849.*

## *B.* Determination of the Sodium Chloride

In a 500 c.c. flask 10 grams of the substance are boiled with about 250 c.c. of water. If marked quantities of sulphate are present, 10% barium chloride solution is now added, slowly and with shaking, until no further precipitation occurs (excess is to be avoided); slight excess of baryta solution is then added to the liquid and the latter boiled for about 15 minutes. With products free from or poor in sulphate, the baryta solution alone is added. When cool, the solution is made up to the mark, mixed and filtered.

100 c.c. of the filtrate (= 2 grams of substance) are heated to boiling in a 200 c.c. flask, ammonium carbonate solution being added gradually and with shaking to the boiling liquid as long as any precipitate forms. The solution is then heated (not boiled) until the precipitate becomes crystalline, and when cold made up to volume with recently boiled water, mixed and filtered.

Of the filtrate, 100 c.c. (= 1 gram of substance) are evaporated to dryness in a platinum dish and the residue gently heated to eliminate the ammonium salts, dissolved in a little hot water and filtered through a small filter. The dish and filter are washed with hot water and the whole of the liquid evaporated to dryness in a tared platinum dish, which is then dried in an oven, heated gently at a dull red, and weighed.

The sodium and potassium chlorides corresponding with 1 gram of substance are obtained in this way. The amount of sodium chloride in the mixed chlorides may be determined by two methods:

1. The potassium is determined as platinichloride or perchlorate (*see* p. 125). $K_2PtCl_6 \times 0{\cdot}307 = KCl$; $KClO_4 \times 0{\cdot}538 = KCl$. This method is preferable when one of the two chlorides greatly predominates.

2. The chlorine in the mixed chlorides is determined volumetrically (by dissolving to a definite volume and titrating an aliquot part of the solution with $N/10\text{-}AgNO_3$ according to Volhard's method), the quantity of NaCl ($x$) being calculated from the formula,

$$x = (p \times 7{\cdot}64632) - (P \times 3{\cdot}63354),$$

in which $p$ = grams of Cl in the mixed chlorides and P the weight of the pure chlorides obtained from 1 gram of the substance.

***

The *strength* (% $K_2O$) of potassium salts is usually guaranteed as follows:
*Kainit*, minimum 12·4, but also 13, 13·5, 14, 14·5 and 15.
*Carnallite*, 9; *high quality carnallite*, 13.
*Sylvine*, minimum 12·4, but also sold up to 16–20.
*Hard salt*, minimum 12·4.
*Potassium chloride*, minimum 56·8 for 90–95% KCl; 50·5 for 80·85% KCl.
*Potassium sulphate*, 51·8 (96% $K_2SO_4$) and 48·6 (90% $K_2SO_4$).
*Potassium and magnesium sulphate*, 25·9.
*Potash manure salts*, 15, 20, 30, 38, 40, 42.

A certain importance as a fertiliser with a potash basis attaches to the potash salt obtained by incinerating residues from the fermentation and distillation of molasses. It consists mostly of potassium carbonate and its strength (% of $K_2O$) is 45–49·5.

# Complex Fertilisers

These include nitrogen-phosphate-potassium fertilising materials such as *stable manure* and other *excrements, guano, dried blood, meat waste, silkworm chrysalides, residues of wool, hair, feathers, leather, horn, nails,* etc., *oleaginous seed cake, peat, various industrial residues* and artificial mixtures of mineral or organic and mineral fertilisers.

Analysis of these products comprises essentially determinations of the moisture, nitrogen, total phosphoric acid and potash, these being carried out by the general methods already described with only such modifications as are indicated below.

## STABLE MANURE

The sample should be taken from many points of the mass and should be mixed without pressing it so as to lose none of the liquid portion.

Analysis is made partly on the product previously dried at 80° and partly on the fresh product.

**1. Water.**—250–500 grams are dried at 70–80° for some hours and then left to cool in the air and weighed. The dried mass is then cut into small portions, chopped and reduced to a fine powder, which is thoroughly mixed again. 10 grams of this are then heated at 105° until of constant weight, the total moisture being calculated.

In order to avoid any loss of ammonia, the total water may be determined as indicated in General Methods, 2.

**2. Ash.**—20 grams of substance dried at 80° and powdered, as in 1, are incinerated at a dull red heat.

**3. Phosphoric Acid and Potash.**—These are determined in the ash; *see* General Methods, 4 and 5.

**4. Nitrogen.**—The ammoniacal nitrogen is determined on the fresh manure, 100 grams of which are distilled with magnesium oxide; the nitric nitrogen by protracted digestion of 500 grams with water, the liquid being subsequently made up to volume and the nitrogen in an aliquot part of the filtrate, corresponding with at least 100 grams of substance, determined by the Schulze and Tiemann method; the total nitrogen, by the Ulsch (or Jodlbaur, if nitrates are present) modification of Kjeldahl's method, on 100 grams of substance previously treated with 200 c.c. of phosphosulphuric acid in the manner described in the following article: Other complex fertilisers, 2.

In each case the procedure is as prescribed under General Methods, 3, *A*, *B*, and *D*.

The composition of *stable manure* varies, in the majority of cases, between the following limits (%): water, 60–80; ash, 5–15 (more frequently, 10–14); total nitrogen, 0·3–0·8, small proportions only being in the ammoniacal condition and very little or none in the nitric state, if the manure is well preserved; phos*phoric anhydride*, 0·2–0·5; and potash, 0·4–1 (usually 0·5–0·6).

## OTHER COMPLEX FERTILISERS

The value of the other complex fertilisers enumerated on p. 136, depends essentially on their nitrogen content, the proportions of phosphoric anhydride and potash being rarely required.

Their analysis includes the following :

**1. Moisture.**—*See* General Methods, 2.

**2. Nitrogen.**—The total nitrogen (organic) is estimated by the Ulsch-Kjeldahl method (*see* General Methods, 3, *C*). With voluminous and non-homogeneous substances (hair, horn, nails, and the like), it is well to heat 50 or 100 grams in a dish on a water bath with 100 or 200 c.c. conc. sulphuric acid or phosphosulphuric acid, the mixture being occasionally shaken, until a homogeneous paste is obtained. This is made up to a definite volume with conc. sulphuric acid and an aliquot part corresponding with 1–5 grams of the original substance, according to the presumed richness in nitrogen, treated in the ordinary way.

**3. Phosphoric Acid, Potash.**—10–20 grams of the substance are charred as indicated in note 1 on p. 124, the phosphoric acid and the potash being then estimated in the well carbonised product as described in General Methods, 4 and 5.

***

*Guanos* may contain, according to their origin : nitrogen, 1–19 ; $P_2O_5$; 1–40 ; and $K_2O$, 0·5–9%. Peruvian guano contains, on the average : N, 7 , $P_2O_5$, 14 ; and $K_2O$, 2%. Italian bat guano (Sardinia) contains about 4% N, 5% $P_2O_5$, and 1% $K_2O$.

In *oil seed cake* (arachis, cameline, colza, cotton seed, linseed, sesamé, etc.) may be found : 2–7% N, 0·5–3% $P_2O_5$, and 0·2–2% $K_2O$.

In *peat* : 0·3–3% N, 0·1–0·8% $P_2O_5$, and 0·1–2% $K_2O$.

Various other organic residues contain about 7–15% N, 0·5–2% $P_2O_5$, and 0·3–1·5% $K_2O$. Exhausted meat residues from meat-extract factories contain 4–11% N, 10–25% $P_2O_5$, and about 0·5% $K_2O$.

## CHAPTER IV

# CEMENT MATERIALS

The principal elements of the more important cement materials are *lime, silica and alumina.*

The raw materials which supply these elements are, more especially: *Limestones*, which contain the lime; *marls*, which contain lime and at the same time silica and alumina; *clays*, *pozzolane* and other similar materials, and blast-furnace *slags*, which contain the silica and alumina.

The cement materials composed essentially of lime are the *fat* and *lean* or *poor limes*. Materials containing, besides lime, marked proportions of silica and alumina (clay), that is, the *hydraulic limes* and the *cements*, have hydraulic properties, setting even under water when properly mixed. Of these the hydraulic limes are poorer in clay than the cements and set more slowly.

*Gypsum*, obtained by burning the hydrated calcium sulphate which occurs abundantly in nature, also occupies a place among the cement materials.

## LIMESTONES AND MARLS

Limestones are rocks composed mainly of calcium carbonate. Their most common impurities are silica and alumina—the constituents of clay—and ferric oxide and alumina; they may also contain small quantities of alkalies, sulphates, sulphides, carbonaceous and bituminous substances and other impurities. Limestones containing marked quantities of clay are termed argillaceous; the name marl is used in cases where the clay is in such proportion that it cannot be regarded as an impurity, the material being a natural and intimate mixture of limestone and clay.

Analysis of these materials aims principally at establishing the amounts of calcium carbonate and argillaceous material present, and in the second place at determining the quantities of the various accessory components.

Such analysis may be partial or complete. The former is far more rapid and is preferred in practice, when determinations are required only of the principal constituents and great accuracy is unnecessary.

## 1. Partial Analysis

This is limited to estimation of the calcium carbonate and any clay present.

The proportion of calcium carbonate may be deduced with sufficient exactness (when only little magnesia is present) by a gasometric determination of the carbon dioxide (*see* later, Complete Analysis, 4) or by the following volumetric method:

1 gram of the powdered material is boiled in a flask with a little water and 25 c.c. of N-hydrochloric acid to expel the carbon dioxide, the excess of acid in the cold liquid being titrated with N-caustic soda in presence of cochineal. The number of c.c. of acid neutralised, multiplied by 5, gives the percentage of calcium carbonate.

If this determination indicates that the proportion of clay present is not negligible, approximate estimation is made of the clay (regarding as such the silica, plus the alumina and ferric oxide). For this purpose 2 grams of substance are treated in a fairly large porcelain dish with about 150 c.c. of water and 10 c.c. of concentrated hydrochloric acid (added carefully), the liquid being boiled for some minutes and the alumina and ferric oxide precipitated, without preliminary filtration, by slight excess of ammonia. The insoluble matter (silica) and the precipitate are then collected on a filter, washed 5 or 6 times with water, dried, ignited at a dull red heat in a crucible and weighed.

## 2. Complete Analysis

For a detailed analysis of a limestone or marl the following determinations are to be made:

**1. Moisture** (hygroscopic water).—5–10 grams of the finely powdered substance are dried in an oven at 105–110° until constant in weight.

**2. Loss on Ignition** (combined water + carbon dioxide + organic matter).—1–2 grams of the dry substance are heated in a platinum crucible, at first gently over a bunsen flame and later for half an hour over a blowpipe flame, this ignition being repeated until no further loss of weight occurs.

**3. Combined Water.**—1–2 grams of the dry substance are heated in a boat in a hard glass tube traversed by a current of dry air, the issuing gas being passed through a calcium chloride tube. The increase in weight of the latter gives the combined water, while the loss in weight of the boat represents the loss on ignition. This determination renders that given under 2 (above) unnecessary.

When organic matter is present, the result of this determination is not very exact, the combined water being increased by that formed by the combustion of the hydrogen of the organic matter.

**4. Carbonic Anhydride.**—This may be estimated gravimetrically or by measuring the gas evolved when the substance is treated with hydrochloric acid.

(*a*) GRAVIMETRIC METHODS. These are based on the loss in weight of

the substance after treatment with hydrochloric acid, or on the increase in weight of an apparatus for absorbing the carbon dioxide generated.

Various forms of apparatus have been designed to determine the loss of weight, one of the most simple being that shown in Fig. 5. It consists of a flask with a doubly-bored stopper, through which pass (1) a bulb tube *a* furnished with a cock and drawn out at the bottom, and (2) a delivery tube terminating in a wider tube *b* containing granulated calcium chloride and a little fused borax. Into the weighed flask a definite weight (about 1 gram) of the substance is introduced, together with a few c.c. of water, the bulb being filled with dilute hydrochloric acid and the upper ends of tubes *a* and *b* closed by rubber tubing and glass rod plug or clip. The whole is fitted together so that all the joints are air-tight and weighed. The upper ends of *a* and *b* are then opened and the hydrochloric acid allowed to flow gradually into the flask, a slow current of air being drawn through the apparatus from *a* to *b*. The tube *a* is next closed and the flask heated gently on a water-bath and afterwards allowed to cool. Dry air is again passed through the apparatus for a few minutes, the tubes then closed and the whole weighed, the loss in weight giving the carbon dioxide in the substance taken.

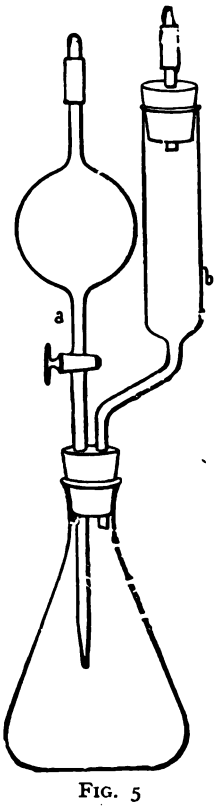

FIG. 5

More accurate is the determination of the carbon dioxide by the increase in weight of an absorption apparatus. This is effected by introducing an exact amount of the substance (about 1 gram) into a flask, adding a little water and closing the flask with a two-holed stopper, through which pass a reflux condenser and a safety tube reaching almost to the bottom of the flask and terminating at the upper end in a tap which can be connected either with a funnel or with a potash apparatus for purifying the air from carbon dioxide. The reflux condenser communicates with a U-tube charged with glass beads and concentrated sulphuric acid, beyond which come first an absorption apparatus consisting of two weighed U-tubes containing soda lime and then an aspirator. Dilute hydrochloric acid is poured on to the substance by means of the funnel, the tap being then closed and the funnel removed. Connection is next made with the potash apparatus, the tap being opened, the aspirator started gently and the flask gradually heated to boiling. Air is passed for at least 15 minutes after heating is discontinued, the absorption tubes being then disconnected and weighed, the carbon dioxide in the substance being thus determined.

If it is likely that the substance contains sulphides, it is well, before the reaction, to add a little mercuric chloride solution to retain the hydrogen sulphide.

(*b*) GASOMETRIC METHOD. One of the best known forms of apparatus

for this method is that of Scheibler and Dietrich, of which the essential features are shown in Fig. 6. It consists of a wide-necked bottle with a perforated stopper by which it is connected with a vertical tube *c*. The latter is joined at the top through a 3-way cock—which can establish communication also with the outside air—with a graduated cylinder *a*, which is connected by a rubber tube at the bottom with a wide tube *b* capable of being raised or lowered at will. All joints must, of course, be quite air-tight.

From 0·5 to 0·6 gram of the substance is placed in the bottle, together with a small tube containing hydrochloric acid, arranged so that, when the bottle is inclined, the acid falls on the substance. The tube *a* is filled with water (coloured red with litmus and a little boric acid, to admit of more easy reading) to the top of the graduations and the pressures inside and outside of it being equalised, the carbon dioxide is liberated by bringing the acid into contact with the substance in the bottle. The pressures are then equalised and the volume of the gas read off, the result being corrected in the usual way.

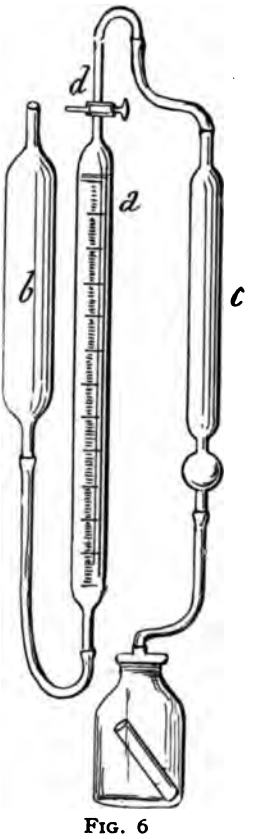

FIG. 6

A more convenient procedure consists in weighing such a quantity of substance—depending on the temperature and pressure and determined by means of special tables [1]—that the volume of gas read off gives directly the percentage of calcium carbonate in the substance.

Of the other forms of apparatus, that of Lunge and Rittener may be mentioned as allowing of increased accuracy.

**5. Organic and Bituminous Substances.**—These are deduced by subtracting, from the loss on ignition, both the combined water and the carbon dioxide, obtainable as under 3 and 4.

**6. Silica.**—(a) *Total silica.* The calcined substance (that remaining after the determination of the loss on ignition) is evaporated to dryness with a little water and hydrochloric acid in a porcelain dish, the insoluble residue being stirred from time to time with a glass rod. It is then kept in an oven for about two hours at 110–115° in order to expel the hydrochloric acid completely.[2] The treatment with hydrochloric acid and the evaporation and the drying in the oven are repeated in order to bring about thorough decomposition of the silicates. The dry residue is then moistened with concentrated hydrochloric acid and left to digest for some hours in the cold. It is then taken up in hot water, the solution filtered and the

[1] *See* Lunge, *Technical Methods of Chemical Analysis* (London, 1908), Vol. I, pp. 661 and 662.

[2] Some consider that the silica is rendered completely insoluble only at 130°.

residue washed by decantation, a few drops of hydrochloric acid and then hot water being added each time. The residue is finally transferred to the filter, dried and ignited in a platinum crucible, the weight representing silica and sand, together with any silicates undecomposed. The *filtrate* serves for the determination of alumina, iron, lime and magnesia (*see* 7 and 8).

(b) *Sand and combined silica.* When the sand is in marked quantity (this is recognized by the fact that the insoluble residue is not perfectly white and scratches when stirred in the dish with a rod), it is of interest to determine it separately from the combined silica. To this end the insoluble residue, obtained as in the preceding case *a* and not ignited, is heated in the porcelain dish with 200 c.c. of 10% sodium carbonate (anhydrous) solution for about an hour on a water-bath. After filtration, the insoluble portion is washed by decantation with hot water, again treated with sodium carbonate solution in the hot, collected on the filter, washed and ignited in a platinum crucible. The weight of this residue represents the sand and any silicates remaining undecomposed.

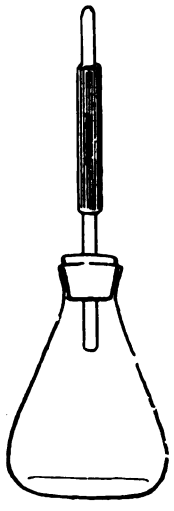

FIG. 7.

In order to make sure that the latter are not in appreciable quantity, the residue is treated in the platinum crucible with a few drops of sulphuric acid and some c.c. of hydrofluoric acid, and evaporated on a water-bath. If necessary, further quantities of hydrofluoric acid are added until all the silica is eliminated and the residue is heated over a small flame to expel the sulphuric acid, ignited and weighed; the amount thus remaining should be negligible.

The sodium solution, containing the combined silica, is acidified with hydrochloric acid, dried on a water-bath and afterwards at 110–115° and taken up in hydrochloric acid, the silica being filtered off and treated as in *a*.

**7. Alumina and Ferric Oxide.**—These are determined together in the filtrate obtained from 6, *a* (determination of total silica). This liquid is heated to boiling in a porcelain dish, any ferrous salts present being oxidised with a few drops of nitric acid, and ammonium chloride and a slight excess of ammonia added. Heating is then discontinued and as soon as the precipitate deposits, it is filtered off, washed at once with boiling water, dried and ignited in a platinum crucible; this gives alumina + ferric oxide. The *filtrate* is used for subsequent determinations (*see* 8).

If the two metals are to be estimated separately, the filtrate obtained in 6, *a* is made up to a definite volume and the two sesqui-oxides together determined in an aliquot part as above. In another aliquot part the sesqui-oxides are precipitated in the same way and the washed precipitate dissolved, while still moist, in hot dilute sulphuric acid, the iron being then reduced to the ferrous state by means of zinc in a flask furnished with a Bunsen valve as shown in Fig. 7. The valve consists of a piece of glass tube passing through the stopper and joined to a rubber tube having a longitudinal slit and closed at the top with a glass plug. When the reduc-

tion is complete and the liquid cold (one drop of it should give no coloration with either potassium ferrocyanide or thiocyanate), it is titrated with standard permanganate solution. The amount of ferric oxide alone is thus obtained.

**8. Lime and Magnesia.**—In the *filtrate* from the aluminium and ferric hydroxides, the lime is determined by acidifying faintly with hydrochloric acid, heating to boiling in a beaker and adding gradually a slight excess of solid oxalic acid (about three times the supposed weight of the lime and magnesia together). Ammonia in excess is then added, with stirring, the precipitate filtered off after some hours, washed with cold water, dried, ignited in a platinum crucible, finally in a blowpipe flame, and weighed as CaO.

In the filtrate from the lime the magnesia is estimated. To this end the liquid is acidified with hydrochloric acid, evaporated if necessary to about 200 c.c. and, when cold, precipitated in a beaker by addition of 40 c.c. of concentrated ammonia and sodium phosphate solution. After at least 12 hours, the liquid is filtered and the precipitate washed with ammonia solution (1 : 5) and dried, the filter-paper being burnt separately from the precipitate and the whole ignited in a porcelain crucible. If the residue is not white, it is treated with a few drops of nitric acid and again calcined, the remaining magnesium pyrophosphate being weighed. $Mg_2P_2O_7 \times 0{\cdot}36207 = MgO$.

**9. Sulphates.**—In some cases limestone contains appreciable amounts of sulphates (gypsum), which may be determined by dissolving a definite weight (about 2 grams) in dilute hydrochloric acid, rendering the silica insoluble in the usual way and removing it by filtration, and precipitating with boiling barium chloride solution. The liquid is left for some hours on a water-bath and the precipitate filtered off, washed, dried and ignited : $BaSO_4 \times 0{\cdot}343 = SO_3$.

**10. Sulphides.**—If the limestone contains also sulphur as sulphides (pyrites, etc.), this may be determined by dissolving a definite weight in hydrochloric acid after addition of a little solid potassium chlorate. The silica is then separated as before and the filtrate precipitated with barium chloride. The excess of the barium sulphate over that obtained as in 9 is derived from the sulphides : $BaSO_4 \times 0{\cdot}13738 = S$.

**11. Other Determinations.**—In rare cases, some other determinations may be required. Phosphoric acid, for instance, is estimated by precipitation of the nitric acid solution with ammonium molybdate, as with fertilisers. Determination of the alkalies is scarcely ever necessary.

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The principal deductions drawn from the results of analysis of a limestone or marl are based on the respective proportions of the principal components, i.e., of calcium carbonate and clay (silica + alumina + ferric oxide). According to the content of clay, distinction is drawn between *limestones*, properly so called, which contain only a minimal amount of clay ; *argillaceous limestones*, in which 10% may be present ; and *marls*, which are described as *calcareous*, with 10–25% of clay, as *marls* proper with 25–50% and as *argillaceous marls*, with more than 50% of clay. With more than 80% of clay, the products may

be regarded as clays proper. These limits are not absolutely fast, passage from one class of substance to another being gradual. The content of clay is not sufficient to give sound indications as to the hydraulic properties of the product resulting from the heating, as these depend also on the method of heating and on the condition in which the separate components occur.

As regards the determination of the accessory components, this gives useful indications when some of them, such as magnesia, sulphur, etc., are present in such quantity as to exert a harmful influence on the quality of the cement products obtained from the materials analysed.

## CLAYS

The essential constituents of clays are silica and alumina, while ferric oxide is also habitually present ; as impurities, they may contain greater or less proportions of calcium and magnesium carbonates, alkali salts, sulphates, pyrites, and small quantities of manganese oxide and titanic acid.

The tests to be carried out on clays vary according to the uses to be made of the latter. Tests for clays to be made into ceramic products, refractory materials, etc., will be omitted, only the chemical analysis of clays for making cements being considered. This analysis includes :

**1. Hygroscopic Water.**—Determined as in limestone.

**2. Loss on Calcination : Combined Water, Carbon Dioxide.**—The loss on calcination is determined as with limestone and usually consists mainly of water. When carbonates or organic substances are present in sensible quantities, the determination of the combined water and carbon dioxide may be made as with limestone.

**3. Silica.**—About 1 gram of the finely powdered, dried substance is weighed exactly, mixed carefully with 4–5 times its weight of dry sodium-potassium carbonate and heated in a roomy platinum crucible over a Bunsen flame, which is kept small at first and is gradually increased later so as to give a semi-fused mass. The flame is then maintained for at least half an hour, the mass being subsequently heated in the blowpipe flame until it is completely fused, the disaggregation thus requiring in all about an hour. When cool, the crucible is placed in a large dish (preferably of platinum) in which it is heated with water on a water-bath to soften the mass, the crucible being afterwards removed with careful washing, and dilute hydrochloric acid gradually added until the carbonates are completely decomposed. The liquid is evaporated to dryness on a water-bath and heated in an oven at 110–115° to render the silica insoluble, the silica being then treated as in limestone and weighed. The *filtrate* serves for the subsequent determinations indicated in 4.

The weighed silica is then evaporated in the platinum crucible with a few drops of sulphuric acid and about 5 c.c. of hydrofluoric acid, gently ignited and weighed : the residue, usually only a few milligrams, consists of alumina, ferric oxide and, maybe, titanic acid, and its weight is subtracted from that of the silica and added to that of the alumina and ferric oxide subsequently found.

To estimate the sand separately from the combined silica, 2–5 grams of the substance are treated with conc. sulphuric acid in a platinum crucible,

most of the acid being then evaporated on a sand-bath and the remainder taken up in water; the clear liquid is decanted off and the insoluble residue digested with hydrochloric acid and then diluted with water and heated, the silica being filtered off and washed. Without being ignited, it is then digested with 10% sodium carbonate solution, the further procedure being as with limestone (*q.v.*, Complete Analysis, 6, *b*).

**4. Alumina, Oxides of Iron and Manganese.**—In the filtrate from the total silica the iron is oxidised with nitric acid and precipitated along with the alumina, as already described (*see* Limestone, Complete Analysis, 7).

If manganese is present in sensible amount, the filtrate from the silica is neutralised with sodium carbonate, treated with neutral concentrated sodium or ammonium acetate solution, diluted with water and heated to boiling for a minute; the liquid is then filtered and the precipitate washed by decantation with boiling water containing a little sodium or ammonium acetate. The precipitate is next redissolved in hydrochloric acid and the aluminium and iron precipitated with ammonia in the ordinary way. The filtrate from the precipitation of the basic acetates is acidified slightly with acetic acid and the manganese precipitated as hydrated peroxide by addition of bromine water to give a brown coloration and then of excess of ammonia, the liquid being heated to boiling until the precipitate separates from the liquid in flocks. After settling, the precipitate is filtered, washed with boiling water, dried and ignited in a blowpipe flame to transform it into $Mn_3O_4$, which is weighed. $Mn_3O_4 \times 0{\cdot}93007 = MnO$.

**5. Lime and Magnesia.**—These are determined in the filtrate from the preceding determination, operating as with limestone (*q.v.*, Complete Analysis, 8).

**6. Alkalies.**—A fresh portion of the substance (2–5 grams) is heated in a platinum crucible on a water-bath with hydrofluoric acid in presence of a little sulphuric acid, the excess of acid being evaporated when all the silica has been expelled. The residue is then taken up in hydrochloric acid and hot water, and the sulphuric acid, aluminium, iron and magnesium precipitated with excess of barium hydroxide at boiling temperature.

From the filtrate the excess of baryta and the lime are eliminated by digestion in the hot with ammonium carbonate and filtration, the filtrate being evaporated to dryness, the residue heated to expel ammonium salts, the residue dissolved in water and the solution filtered and evaporated to dryness in a tared platinum dish. This residue consists of the chlorides of any sodium and potassium present.

If required, the separate determination of the two alkali metals may be carried out by the indirect volumetric method (titration of the total chlorine in a known weight of the chlorides; *see* Fertilisers, p. 135) or by the gravimetric method (precipitation of the potassium as platinichloride), the procedure being as described with fertilisers (p. 124).

**7. Sulphates, Sulphides.**—These are determined as with limestone (*q.v.*, Complete Analysis, 9 and 10).

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**The deductions to be drawn from the composition of a clay, in so far as these are of interest in the manufacture of cement, are based (1) on the proportions**

of the essential components, namely, silica, alumina and ferric oxide (the sum of which is not less than 80%), in order that it may be calculated in what ratio it must be mixed with the other raw materials, and (2) on the amounts of lime and other impurities which may be harmful to the cement.

## POZZOLANE AND SLAGS

True *pozzolane* are readily friable, volcanic materials which, when mixed with lime, form mortars capable of setting even under water. Their essential components are silica, alumina and ferric oxide, and they contain also lime, magnesia and alkalies, together with a considerable amount of combined water. The more important and the best known are (1) those from the neighbourhood of Rome, which are distinguished as red (brownish red or violet red), black (dark brown or grey) and pozzolanelle (greyish or reddish, of more recent formation), and (2) those from near Naples, which are usually light grey but sometimes dark grey. Pozzolane are also found in the Auvergne and other volcanic regions. With the pozzolane are grouped other similar materials, such as *santorin*, found in the island of that name and in other Greek islands, and *trass*, which occurs in the Eifel and in other districts on the banks of the Rhine; both of these are greyish. There are also *non-volcanic pozzolane*, composed of the detritus of various siliceous rocks, but their use is somewhat limited.

The name *artificial pozzolane* is given to substitutes for pozzolana; these are obtained by calcination of clay, schist, basalt, etc., but use is made principally of blast-furnace *slag*, which is granulated by pouring it into water direct from the furnace.

The testing of pozzolane and slags includes quantitative chemical analysis and, especially for pozzolane, certain technical tests indicated below.

### 1. Chemical Analysis

Chemical analysis of pozzolane and slags may be made by the methods already described for the analysis of clays, determinations being made of the moisture, the loss on ignition, the silica, alumina and ferric oxide (also any manganese oxide), lime, magnesia, alkalies (also any sulphates and, especially in slags, sulphides). As regards the loss on ignition, in good pozzolane this is composed almost entirely of the combined water, since carbon dioxide is not usually present in appreciable quantity. The combined water is an important factor with the pozzolane, standing in close relation to their hydraulic properties.

Further, in some cases, it is necessary to determine the constituents of the silicates of pozzolane attackable by hydrochloric acid and of those non-attackable. In this event, 2–4 grams of the substance are treated with hydrochloric acid in the same way as the limestones and marls (*q.v.*, Complete Analysis, 6, *a*). The undecomposed residue will contain the sand, the undecomposed silicates and the silica of the silicates which have been attacked; the bases corresponding with the last are found in the filtrate

and are determined by the method already described (*see* Limestones, Complete Analysis, 7 and 8). By treatment of the insoluble residue with sodium carbonate (*see* Limestones, Complete Analysis, 6, *b*), the silica of the silicates attacked by the acid is separated. The new residue is disaggregated and examined by the methods given for clays (*q.v.*, 3–6) the silica and the different bases of the silicates not decomposed by hydrochloric acid thus being determined.

Another determination of use in the evaluation of pozzolanic materials is that of the constituents of the silicates attackable by alkalies by Lunge and Millberg's method.[1] Pozzolana and trass contain, as active components, zeolitic silicates, especially a silicate of aluminium and sodium analogous to analcite, these being decomposed in the hot by caustic potash. Thus, by digesting 0·5 gram of the substance with 50 c.c. of 30% caustic potash solution for about 6 hours on the water-bath, diluting, filtering and determining the silica and alumina in the filtrate, an indication is obtained of the technical value of the material. The experiments of the authors mentioned above on various specimens of trass and pozzolana show that about 24-28% of silica and 11-13% of alumina pass into solution under this treatment.

## 2. Technical Examination of Pozzolane

This includes: certain preliminary tests for detecting the presence of heterogeneous and inert material; the lime absorption test, and especially tests relating to the fineness, the absolute and apparent density, the setting and the strength.

**1. Presence of Extraneous Matter.**—The presence of earthy matters may be detected by shaking the pozzolana with water and allowing to settle: pozzolana free from earth deposits rapidly and leaves the liquid clear. When the pozzolana is heated with caustic potash solution, if earthy matter is present, the organic substances of the latter colour the potash solution brown, and the addition of acid then produces a brown precipitate. Further, on dry distillation, nitrogenous organic matter yields empyreumatic products, alkaline owing to the presence of ammonia; a pozzolana containing them will give, therefore, ammonia when heated with caustic potash solution.

**2. Lime Absorption.**—This test yields satisfactory results if a control test on a good pozzolana of known value is also made. A 10% sugar solution is left in contact with an excess of spent lime for at least 12 hours, with frequent shaking. After filtration, the alkalinity of the solution is determined by means of N-hydrochloric acid, of which 1 c.c. = 0·028 gram CaO.

The test is made by treating 20 grams of pozzolana in a flask with 100 c.c. of the above solution, closing the flask and leaving it for two or three days, with occasional shaking; the liquid is then filtered through a dry filter and an aliquot part titrated with N-hydrochloric acid. The quantity of calcium oxide absorbed by 100 grams of the pozzolana is then calculated.

[1] *Zeitschr. für angew. Chem.*, 1897, p. 428.

This quantity usually varies between 1 and 2 grams and is greater with the better pozzolane.

**3. Granularity and Fineness.**—With pozzolane in the natural granular condition, the degree of granularity is determined by using a series of sieves with meshes measuring 5, 4, 3, 2, 1·5, 1 and 0·5 mm., 2 grams of material being taken and the results expressed as percentages (of the total weight) not passing through each sieve. With powdered pozzolana, however, the fineness of grinding is determined in the way indicated later for cements.

This procedure, and also the ones described under 4, 5, 6 and 7, are those prescribed in the *Official Italian Regulations and Conditions*, approved by the decree of the Minister of Public Works, June 13, 1911.

**4. Specific Gravity.**—The specific gravity (absolute density) is determined on the powdered material, dried and passed through a sieve of 900 meshes per sq. cm., by the methods indicated later for cements.

**5. Apparent Density.**—This is the weight of 1 litre of the material poured without compression. With granular pozzolane it is determined after the latter has been dried and passed through a sieve with round orifices 3 mm. in diameter, the same apparatus and procedure being used as with cements, excepting that the plate in the funnel has apertures 3 mm. instead of 2 mm. in diameter. With powdered pozzolane, however, the apparent density is determined exactly as with cements. The result is expressed in grams per litre (or kilos per cub. m.).

**6. Setting Test.**—The procedure is different for granular or powdered pozzolana.

In the former case the pozzolana should be previously dried in the oven until of practically constant weight and then passed through a sieve with circular holes 3 mm. in diameter. Common lime (with at least 95% CaO) is hydrated by sprinkling it with water, being afterwards left for a fortnight in a moist place and sieved to remove uncombined or inert particles. A *normal mortar* is then prepared from 1 part of the powdered slaked lime and 3 parts of the pozzolana prepared as above ; the manipulation is carried out at a temperature of 15–20° on a marble slab by means of a trowel, the components being mixed at first dry and then with ordinary water, this being gradually added until a homogeneous, plastic mass is obtained which agglomerates under the pressure of the hand.

This mortar is used to fill two zinc plate cylindrical moulds, 10 cm. in diameter and 5 cm. in height, which are kept in a moist atmosphere, the setting tests being commenced after 48 hours and repeated every 24 hours. In this test use is made of a Vicat needle similar to that described later for cements but with a total weight of 1 kilo and of rather different dimensions : the point of the needle is somewhat conical, the length being 40 mm., and the diameter 3·2 mm. at the base and 1·66 mm. at the apex. The needle is allowed to fall from a height of 30 mm., and hardening is considered to begin when the needle does not penetrate more than 7 mm. into the mortar. At this point, one of the mortars is placed in water and the other kept in *the moist* chamber, the periodical tests being continued on both and the

results given graphically in a diagram (days as abscissæ and penetration of the needle in mm. as ordinates).

In the second case, that is with powdered pozzolane, the mortar is prepared from 1 part of powdered slaked lime and 4 parts of the pozzolana, these being mixed first dry and then with water; the consistency of the mortar and the setting are tested by methods indicated later for cements.

**7. Strength.**—Tensile and compression tests are carried out as with cements.

With a granular pozzolana, the moulds are filled by hand by means of a spatula with the mortar prepared as for setting tests; after some days, when the briquettes have attained a certain consistency, they are removed from the moulds and kept first in the moist chamber until 7 days after mixing and subsequently some in water and some in moist air. The strength test is made after 28 days and may be repeated after 84 days, 210 days and 1 year.

In the case of powdered pozzolana, a normal mortar is prepared from 1 part of the lime-pozzolana mixture (1 of lime and 4 of pozzolana) and 3 parts of normal sand (*see* later: Cements), the procedure for filling the moulds and carrying out the tests being the same as for cements.

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The chemical compositions of some of the better known *pozzolane*, santorins and trass are given in Table IV.

Pozzolane should be free from extraneous and inert substances and for the measurements, both by weight and by volume, they should not contain more than 10% of moisture.

Pozzolane are regarded as *energetic* when, in the natural granular state, they answer the following requirements: (1) the normal mortar (3 parts by weight of pozzolana to 1 of lime), after 7 days in the moist chamber, does not allow the Vicat needle weighing 1 kilo to penetrate more than 7 mm. when falling from a height of 30 mm.; (2) after 28 days—7 in moist air and 21 in water—the briquettes of normal mortar exhibit a tensile strength of not less than 4 kilos per sq. cm. and a compression strength of at least 20 kilos per sq. cm.

*Feeble* pozzolane are those yielding normal mortars which do not attain the above strength but allow, after 7 days, the needle to penetrate not more than 10 mm., and after 28 days exhibit tensile and compressive strengths of 2 and 10 kilos per sq. cm. respectively. If these standards are not attained, the material is not regarded as pozzolanic in character.

*Slags*, to be of use in the cement industry, should be basic, that is, the ratio $CaO : SiO_2$ should be not less than 1, and they should be as rich as possible in alumina and as poor as possible in manganese, magnesia and sulphides. The composition of a good slag should lie between the limits: $SiO_2$, 25–36%; $Al_2O_3$, 10–22%; $Fe_2O_3$, up to 1·5%; FeO, up to 2%; MnO, up to 3%; CaO, 30–50%; MgO, up to 3%; $CaSO_4$, up to 2%; and CaS, up to 3%. Alkalies are usually present in small quantity.

TABLE IV

## Compositions of Pozzolane and the like

| Quality. | Loss on Ignition. | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | Remarks. |
|---|---|---|---|---|---|---|---|---|---|
| Rome (S. Paolo). Red | 8·46 | 45·50 | 15·12 | 12·05 | 9·34 | 3·59 | 3·78 | 2·15 | 52·71% soluble in HCl |
| Do. do. Do. | 10·40 | 46·15 | 23·19 | 6·42 | 8·52 | 2·25 | 3·01 | | 25·52% ,, ,, |
| Do. (Cas Caffarella). Black | 11·90 | 46·85 | 21·49 | 5·21 | 8·54 | 0·96 | 4·68 | | 25·66% ,, ,, |
| Do. (Via Ardeatina). Pozzolanella | 9·40 | 47·50 | 28·38 | 3·68 | 5·03 | 1·36 | 4·60 | | 27·18% ,, ,, |
| Do. (Portonaccio). Red [1] | — | 53·84 | 23·91 | 10·00 | 8·78 | 0·84 | 1·66 | 0·90 | — |
| Do. (Pratolungo). Red | 6·10 | 46·24 | 19·26 | 11·18 | 9·82 | 2·84 | 2·66 | 2·77 | — |
| Do. (Salone). Black [1] | — | 46·39 | 26·16 | 7·76 | 10·28 | 3·53 | 0·66 | 5·18 | — |
| Do. (Vicovara). Black [1] | — | 46·34 | 24·27 | 9·74 | 9·83 | 2·20 | 1·59 | 5·20 | — |
| Viterbo. Red [1] | — | 48·06 | 20·58 | 11·78 | 11·28 | 2·83 | 2·85 | 2·58 | — |
| Sulmona (Portella). Grey [1] | — | 57·02 | 35·31 | 4·24 | 3·21 | — | 0·13 | — | — |
| Naples (Bacoli). Light grey | 7·25 | 52·77 | 17·00 | 4·84 | 3·28 | 1·35 | 4·94 | 7·65 | — |
| Do. do. Do. [1] | — | 64·71 | 20·03 | 4·98 | 4·39 | 0·96 | 1·77 | 3·07 | — |
| Do. (Torre d. Greco). Dark grey | 2·21 | 47·10 | 21·90 | 8·01 | 9·91 | 1·56 | 2·56 | 6·01 | — |
| Do. do. Do. [1] | — | 49·54 | 19·91 | 10·02 | 12·07 | 3·34 | 2·50 | 2·25 | — |
| France (Auvergne) | 4·10 | 53·20 | 8·70 | 9·00 | 23·10 | — | 1·20 | | 66·3% soluble in HCl |
| Do. (Hérault) | 12·40 | 54·50 | 18·90 | 6·80 | 2·80 | 1·10 | 3·00 | | 56·5% ,, ,, |
| Santorin | 1·50 | 64·34 | 10·88 | 6·44 | 3·62 | 2·77 | 6·05 | 4·83 | 15·8% ,, ,, |
| Do. | 4·06 | 66·37 | 13·72 | 4·31 | 2·98 | 1·29 | 4·22 | 2·83 | 3·5% ,, ,, |
| Trass from Andernach [1] | — | 59·70 | 20·85 | 4·42 | 1·77 | 1·29 | 5·98 | 4·96 | — |
| Do. do. Hersfeldt | 12·04 | 54·96 | 21·52 | | 2·08 | 1·60 | — | — | 40·4% ($SiO_2+Al_2O_3$) soluble in 30% KOH solution |
| Do. do. Burgbrohl | — | 56·22 | 24·92 | | 2·10 | 1·08 | — | | 36·7% ($SiO_2+Al_2O_3$) soluble in 30% KOH solution |

[1] These results refer to the calcined substance.

# LIME

This is the product of the calcination of limestone and, when mixed with siliceous sand, forms the well-known *common mortar*. Limes are distinguished as *fat limes*, consisting essentially of calcium oxide and readily slaked with evolution of considerable heat and with increase of volume, and *poor limes*, containing marked quantities of clay, magnesia and other impurities.

The chemical analysis of lime is analogous to that of limestone (*see* Limestones and Marls), but usually the determination of carbon dioxide is unnecessary. For industrial purposes, however, certain technical tests generally suffice, these being principally:

**1. Ease of Storage.**—This is deduced from the greater or less time required for a lime exposed to the air to become slaked and fall into powder in contact with the moisture of the air.

**2. Ease of Slaking.**—This is ascertained by observing if the lime, mixed with 3–4 times its weight of water, undergoes hydration in a short time with pronounced generation of heat and formation of a dense paste.

**3. Volume after Slaking.**—This is determined by means of the Michaëlis volumenometer, consisting of a brass vessel into the orifice of which a glass tube with graduations starting from 200 c.c. may be screwed air-tight. In the container a piece of the lime weighing 25–50 grams is slaked with the amount of water necessary to obtain a dense paste, heat being applied, where necessary, by a water-bath and also occasional stirring until cracks begin to develop in the paste. The latter is then allowed to cool, the graduated tube fitted, 200 c.c. of water introduced from a pipette, and the volume read.

Another method, based on the use of a porous cylinder and capable of giving good results, has been described by G. Giorgis and G. Cenni.[1]

In practice, owing to the difficulty of obtaining a small sample representing the bulk of a lump lime, a large quantity of the substance (at least 5 kilos) is sprinkled with water, left in the air for at least two days, after which water is added to give a paste which can be poured, this being then introduced (through a sieve to retain inert matter) into a bucket of known dimensions; after the excess of water has been separated from the surface of the paste, the level of the latter is read off and its volume calculated.

***

Fat lime for the production of mortar should be of recent and thorough kilning, and not powdery or effloresced; it usually contains not less than 95% CaO, mostly free. It should be non-vitreous and of uniform colour, and when mixed with the necessary quantity of water it should undergo rapid slaking with transformation into a firm paste, without leaving any appreciable residue due to insufficiently burnt, siliceous or otherwise inert matter; the yield is usually not less than 2·5 cub. dm. of paste per kilo of quicklime.

[1] *Annali di Chim. applicata*, 1915, III, p. 175.

## HYDRAULIC LIMES AND CEMENTS

The chief of these products are furnished by the kilning of argillaceous limestone or marl or mixtures of these with each other or with clay. Among them are : *Hydraulic lime*, which is whitish or yellowish and causes sneezing when its powder is diffused sparsely in the air ; *natural rapid-setting cement* or *Roman cement*, dark yellow or greyish yellow ; *natural slow-setting cement* or *natural Portland cement*, and *artificial* (or *true*) *Portland cement*, dark grey, often inclining to greenish. Other forms of cement are *Grappier's cement*, made from the argillaceous residues from the slaking of hydraulic lime, and of whitish colour ; *slag cements*, intimate mixtures of blast-furnace slag with lime, grey in colour, and *mixed cements*.

The testing of these products includes chemical analysis and, what is of greater practical importance, certain technical tests described later.

### 1. Chemical Analysis

The more important determinations to be made with hydraulic limes and with cements are : loss on ignition (water plus carbon dioxide), total silica, alumina plus ferric oxide, lime and magnesia. In some cases estimations are required of the carbon dioxide, the sand separately from the combined silica, ferric oxide separately from alumina, sulphates (gypsum) and, in slag cements, sulphides (calcium sulphide). All these determinations are made by the methods already described in considering limestones and marls.

Sometimes, in order to detect the *presence of heterogeneous materials* (e.g., of slag in a Portland cement), it is convenient to analyse separately the finer parts (passing through a sieve with 4,900 meshes per sq. cm.) and the coarser ones : any appreciable difference indicates addition of extraneous material.

To the determinations mentioned above, that of the *alkalinity* (free lime), carried out as follows, is sometimes added : 1 gram of the finely powdered material is shaken for 10 minutes with 100 c.c. of distilled water and filtered, 50 c.c. of the filtrate being titrated with N/10-hydrochloric acid.

From the results of the chemical analysis it is usual to calculate the relations between the principal components. The *hydraulic index* is the ratio, (silica + alumina) : lime ; according to some, the ferric oxide also is added to the alumina, while, according to others, the magnesia should be added to the lime, owing to analogous functions in the setting. The *hydraulic modulus* of Michaëlis is the inverse ratio, namely, lime : (silica + alumina + ferric oxide).

### 2. Technical Tests

The chief of these are as follows :

**1. Ocular Examination.**—This is made with a lens and may detect the presence of extraneous matter, such as particles of coal, sand, slag, gypsum, etc.

**2. Methylene Iodide Test.**—This serves to separate the extraneous matters accompanying a cement and is based on their different densities. It applies especially to Portland cement and is carried out by shaking a small quantity of the cement with a solution of methylene iodide in benzene or oil of turpentine of density 3 [1] and allowing to stand. The cement particles are the heavier and settle, whilst the extraneous matters float.

When a more complete separation is required, methylene iodide solutions of densities 3·05, 3·00, 2·95 and 2·70 are successively used. What sinks in the first solution consists of pure Portland cement ; that of density between 3 and 3·05 is not quite pure cement, that between 2·95 and 3 is mixed cement and slag, and that between 2·70 and 2·95 pure slag ; that floating in the solution of density 2·70 may be coal, ash, gypsum, and the like. The separate fractions may be examined to ascertain their nature.

**3. Specific Gravity.**—This may be determined with the picnometer, using benzene or benzine as liquid. Use is also largely made of Schumann's volumenometer, which consists of a bottle, in the neck of which is ground a glass tube graduated in tenths of a c.c. The bottle is filled with the benzene or benzine to the commencement of the graduation and the division to which the liquid reaches read ; 100 grams of cement (or lime) are then introduced into the bottle, which is tapped gently to make the air-bubbles rise, the new level of the liquid being then read.

A more convenient volumenometer is that of Le Chatelier, which comprises a bulb of about 120 c.c. capacity, terminated by a neck 0·20 metre high with an expansion measuring exactly 20 c.c. between two marks ; above the upper mark the tube is graduated from 0 to 3 c.c. in tenths. When the apparatus is full of benzene to the lower mark, a definite weight of the cement (64 grams of Portland cement may be used or 60 grams or less of a lighter product) is introduced by means of a funnel reaching just below the upper mark. The increase in volume represents the volume occupied by the cement.

According to the *Official Italian Regulations and Conditions*,[2] the specific gravity (absolute density) of hydraulic agglomerants may be determined by any method provided it allows of an accuracy of two units in the second decimal figure ; it should be determined on the material after previous drying and powdering so as to pass through a sieve of 900 meshes per sq. cm., and the temperature of the apparatus, material and liquid during the determination should be about 15°.

**4. Apparent Density.**—This is the weight of a litre of the material poured without compressing. To determine it, the cement is gradually introduced through a funnel into a litre cylinder 10 cm. high until the cylinder is not only completely filled but heaped up. The excess is then removed by drawing a straight strip, held vertically, across the top of the cylinder, which is then weighed. The weight thus found, less the tare, gives the apparent density.

According to the *Official Regulations* (Italian) already mentioned, the funnel to be used for filling the cylinder is 20 mm. in diameter at the base and 150 mm.

[1] The density of methylene iodide is 3·33 at the ordinary temperature.

[2] Approved by the decree of the Minister of Public Works, January 10, 1907.

at a point 150 mm. above the base; at this height is fixed a perforated disc with about 1050 holes 2 mm. in diameter per sq. dm. The funnel is prolonged into a cylindrical tube 20 mm. in diameter and 100 mm. long, the lower extremity being 50 mm. from the top of the cylinder beneath. The material to be tested is poured on to the perforated disc in quantities of about 300 grams at a time, and is stirred with a wooden spatula 40 mm. wide to assist the passage through the holes. During the filling care must be taken not to shake the apparatus. The mean of three consecutive results is taken as the true value.

Some authorities advise determination of the litre-weight of the cement when compressed by a definite number of blows (generally 1000).

**5. Fineness of Grinding.**—This is determined by sieving the material through successive metal wire sieves and weighing the residue on each sieve. Use is generally made of sieves of 900–4900 meshes per sq. cm., made of wires of diameter 0·15 and 0·05 mm. respectively. The test is made on a 50 gram sample, the results as percentages being obtained by adding two results obtained with the same sieve. The sieving is conducted by hand, and is regarded as complete when 25 successive shakings do not cause more than 0·1 gram of material to pass through the sieve. The results are expressed by adding, for each sieve, the weights of the residues not able to pass through it.

**6. Quantity of Water for Pasting (gauging).**—The quantity of water required to give a paste of normal consistency (*normal paste*) is measured as follows: 400 grams of the material are placed on a marble or zinc slab in the form of a heap hollowed in the middle. Into this is poured, in one lot, the whole of the water considered necessary at 15–20°, the whole being mixed rapidly with a trowel, for one minute with a rapid-setting cement or for three minutes with a slow-setting cement or a hydraulic lime (in any case for a less time than is required for setting to begin: *see* below).

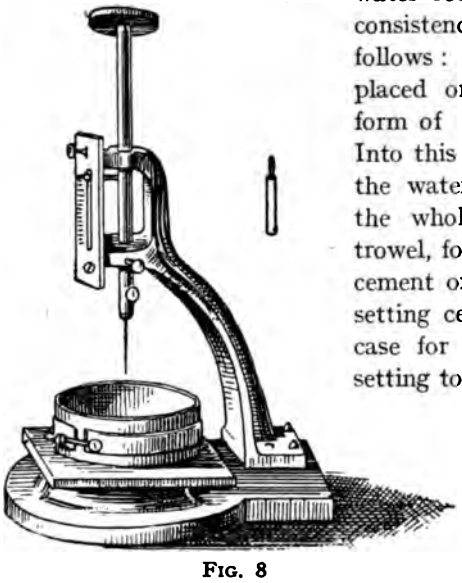

FIG. 8

With the same trowel the paste is immediately filled into a split cylindrical metal or ebonite mould, 4 cm. high and 8 cm. in diameter on a smooth glass plate; the surface of the cement is smoothed with the trowel, care being taken to avoid compression. The *Tetmajer rammer* is then allowed to descend into the mortar by its own weight (300 grams). This rammer consists of a small cylinder, 1 cm. in diameter, which replaces the needle of the Vicat apparatus (Fig. 8). The consistency is normal when the cylinder comes to rest with its base about 6 mm. from the level of the glass plate, as indicated on the scale. If the consistency is not normal, the test is repeated with a different quantity of water. The proper amount of water used is divided by 4 to give the quantity per 100 grams of material.

**7. Setting Time.**—This is determined on the normal paste, and that used in the preceding test may be used, being kept during the whole of the tests in a moist chamber at about 15°. The test is made with *Vicat's needle* (Fig. 8), which is a cylindrical steel needle of 1 sq. mm. section (1·13 mm. diameter), cut normally to the length and weighing, with the rest of the moving parts, 300 grams. It is brought gently into contact with the mortar to ascertain if it penetrates. The test is repeated at first every minute and afterwards at gradually increasing intervals. The *initial set* is taken as the time when the needle fails to reach the bottom of the test-piece and the *final set* as that when the needle fails to enter to an appreciable extent (about 0·1 mm.); times are measured from the moment when the water is added to the cement for the gauging.

This procedure is that adopted by the *Official Italian Regulations*. When setting is almost complete, it is well to detach the mould from the glass and test on the lower surface of the mortar where it is more polished and homogeneous; with slow setting, it is useful to cover the mould with a glass to prevent drying. Some advise, especially with very slow-setting products, the determination of the time of setting under water.

The rise of temperature of the mortar during setting may give useful indications and is ascertained by means of a thermometer with its bulb immersed in the paste; temperature readings are taken at regular intervals and the temperature-time curve traced.

**8. Strength.**—Only a brief reference will be made to these mechanical tests, which are not usually made in chemical laboratories. Chief among them are those of *tensile* and *compression strengths*.

According to the *Official Italian Regulations*, such tests are made in some cases on a normal paste of the pure cement (*see* above, 6), but usually on a *normal mortar* obtained by making an intimate mixture of 1 part of the agglomerating material with 3 parts of sand and preparing a paste from this and the necessary amount of water, to be determined by trial (usually about 8% by weight of the mixture). The granules of the *normal sand* to be used must pass through circular holes 1·5 mm. in diameter but not through 1 mm. holes.

For tensile measurements briquettes are moulded in the shape of the figure 8 and of definite form and dimensions, the minimum section in the narrowest part being 5 sq. cm. The mortar is compressed into the mould by 120 blows, delivered during 3 minutes, of a hammer weighing 2 kilos falling from a height of 0·25 metre and developing energy amounting to 0·30-kilogram-metre per gram of dry substance. The briquette is then removed from the mould. The tests are usually made after 28 days (or 7 with rapid-setting cements), during the first of which (or the first two with hydraulic limes) the briquettes are kept in moist air and during the remainder in water. In some cases measurements are made after different periods (in general, the strength after 28 days is about two-thirds of the value after 1 year). The results are expressed in kilos per sq. cm. of the minimal section and for a given material six briquettes are tested and the mean of the four highest results taken.

With pure cement, the briquettes are made by hand with the help of

a trowel and are taken from the moulds after 24 hours, when they are immersed in water.

Greater value attaches to the results of compression tests. According to the *Italian Regulations*, cubical briquettes of 50 sq. cm. face are made in suitable moulds by compressing with 160 blows from a 3 kilo hammer falling 0·5 metre and developing 0·30 kilogram-metre per gram of dry substance. The briquettes are kept and the results expressed as with tensile strength, the same being the case with briquettes of pure cement. The compressive stress should be exerted on two opposite faces which have been in contact with lateral walls of the mould.

*Bending* tests are also sometimes made, and for practical purposes, tests of the *indeformability* or *constancy of volume* in the cold and in the hot are of importance. Further, in some cases, it may be advisable to make tests of *adhesion*, *porosity* and *permeability*. For these tests and for greater details of the compression and tension tests, reference must be made to special treatises.

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*Hydraulic limes* have the specific gravity 2·5–2·9 or, more commonly, 2·7–2·85, and their apparent density is usually 0·5–0·8, and may be even greater with those having very marked hydraulic properties. The chemical composition varies somewhat, but in ordinary cases the proportion of clay is 20–30%. The hydraulic index may vary between fairly wide limits, but in most instances is less than 0·50. The loss on calcination is usually 8–12% but may reach 20% or more ; as regards alkalinity, the solution obtained from 0·5 gram of substance requires about 20 c.c. of N/10-acid. For a paste of normal consistency, hydraulic limes almost always require more than 40% and sometimes even 60% of water ; setting, in either air or water, seldom takes place in less than a day, and often takes longer.

According to the *Official Italian Regulations*, hydraulic lime should have a specific gravity of at least 2·7 and should not leave more than 7% of residue on a sieve of 900 holes per sq. cm. and not more than 25% on one of 4900 holes ; the setting of the normal paste should not begin earlier than 6 hours and should not end later than 48 hours. The strength of the normal mortar briquette after 28 days should not be less than : tension, 5 kilos per sq. cm. for ordinary hydraulic lime and 8 for those with marked hydraulic qualities ; compression, 25 kilos and 50 kilos per sq. cm. respectively.

*Natural cements* usually have the specific gravity, 2·8–3, and the apparent density 0·7–1 for quick-setting, and sometimes as much as 1·2 for slow-setting cements. The hydraulic index is usually 0·50–0·80 or more, and is greater with quick-setting than with slow-setting products (with the former, the Michaëlis hydraulic modulus is generally 1·2–1·6). The loss on ignition and the alkalinity are almost always less than with the hydraulic limes. At the most 30–45% of water is required for the normal paste and setting requires less than half an hour for quick-setting and more than half an hour—sometimes some hours—for rapid-setting cements. Semi-slow-setting cements are sometimes regarded as an intermediate grade, but the transition from rapid- to slow-setting cements is too gradual to allow of the definition of the limits of such a class.

For *rapid-setting cements* the *Official Italian Regulations* prescribe : a specific gravity greater than 2·8 ; not more than 20% of residue on a 900 mesh sieve ; initial and final sets to occur between 1 minute and 30 minutes ; briquettes of normal paste to exhibit, after 7 days, tensile and compressive strengths not less than 16 and 160 kilos respectively per sq. cm.

True *Portland cement* has the specific gravity 3·05–3·25 and the apparent

density 1·1–1·3 or, after compression caused by 1000 shakes, about 1·8. The chemical composition is moderately constant ; the loss on ignition never reaches 5% and usually does not exceed 3% ; the alkalinity is somewhat less than in limes, only 4–6 c.c. of N/10-acid being required per 0·5 gram of substance. The essential components usually vary between the following limits :

| | |
|---|---|
| Silica | 19–26% |
| Alumina | 4–10 |
| Ferric oxide | 2–4 |
| Lime | 57–67 |

The hydraulic index usually lies between 0·42 and 0·50 but may reach 0·60, and the Michaëlis hydraulic modulus varies between 1·7 and 2·2, its mean value being about 2. According to Le Chatelier, the proportion of lime should be such that, when the components are expressed in chemical equivalents, the ratio

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3}$$ is less than 3, and $$\frac{CaO + MgO}{SiO_2 - (Al_2O_3 + Fe_2O_3)}$$ is greater than 3.

As regards the accessory components, good Portland cement should not contain more than 3% of MgO or 1·2% of $SO_3$, or sulphides in appreciable quantity. This cement requires 27–30% of water for gauging and usually sets in a few hours.

The *Official Italian Regulations* prescribe for Portland cements : specific gravity not less than 3·05 ; not more than 2 (or 20)% of residue to remain on a sieve of 900 (4900) meshes per sq. cm. ; initial set of the normal paste to occur later than 1 hour and final set between 5 and 12 hours ; after 28 days, the strength of the normal mortar briquettes to be not less than 20 and 220 kilos respectively per sq. cm. towards tension and compression.

*Slag cements* have an apparent density usually less than 1 and a specific gravity 2·6–2·8, the values for *Grappier's* cements being 0·8–1·1 and 2·8–3 ; *mixed cements* approach one or the other class, according to their composition. All these cements require 30–40% of water and set after some hours, almost always before 24 hours. As regards their chemical composition, slag cements contain calcium sulphide in appreciable amount, which may reach or surpass 3–4%, and they are usually richer in alumina and poorer in lime than Portland cements. Grappier's cements are, however, poor in alumina and rich in silica, of which they contain 22–30% ; the loss on ignition is generally less than with hydraulic limes and mostly about 5%. Another characteristic of Grappier's and slag cements is the fineness of grinding : they leave almost no residue on the 900-mesh sieve and usually not more than 10% on the 4900-mesh.

Mention must be made of the so-called *sand cements*, which are used, especially in America, for street paving, dykes, aqueducts and canals, and have recently been introduced into Italy. They consist of intimate mixtures of Portland cement and siliceous rock (sand, arenaceous deposit, granite, etc.) which are ground together and are moderately rich in silica and unattackable silicates (42% or more).

Tables V, VI and VII contain examples of the compositions and properties of hydraulic limes and cements.

## GYPSUM

Ordinary gypsum is obtained by heating hydrated calcium sulphate at a moderate temperature and is composed essentially of calcium sulphate still containing a part (about one-fourth) of the water of crystallisation. The principal impurities which may be present are clay, oxide of iron, calcium carbonate, sand, and sometimes pyrites and bituminous matter.

TABLE V

## Compositions of Hydraulic Limes

| | Quality. | Gauging Water. | Time of Setting. | Loss on Ignition. | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | Hydraulic Index (the $Fe_2O_3$ being included with the $Al_2O_3$ where they were not determined separately). | Author. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| French. | Le Teil (4 samples). . | — | — | 8·60–14·73 | 21–23·45 | 0·76–3·19 | 0·66–0·83 | 59·80–64·85 | 0·30–1·44 | 0·42–0·63 | 0·38–0·41 | Candlot |
| Do. | Beffes (2 samples) . . | — | — | 14·90–16 | 16·20–16·30 | 4·11–5·41 | 2·09 | 58·90–60·36 | 0·54–1·15 | 0·77–0·90 | 0·33–0·37 | ,, |
| Do. | Tournai (4 samples) . | — | — | 8·75–13·40 | 19·30–22·20 | 3·30–4·44 | 1·16–2·00 | 58·50–63·32 | 0·60–1·51 | 0·45–0·72 | 0·37–0·43 | ,, |
| Do. | Do. (1 sample). . | — | — | 24·00 | 10·20 | 4·32 | 1·88 | 58·12 | 1·11 | 0·34 | 0·25 | ,, |
| Do. | Do. (1 sample). . | — | — | 8·10 | 25·80 | 5·65 | 1·57 | 57·50 | 0·68 | 0·90 | 0·55 | ,, |
| Do. | Sauveterre . . . . | — | — | 15·80 | 15·10 | 5·00 | 1·80 | 57·00 | 3·90 | 1·40 | 0·35 | ,, |
| Do. | Seilley . . . . . | — | — | 12·10 | 18·90 | 6·23 | 1·87 | 58·75 | 1·29 | 0·54 | 0·42 | ,, |
| Do. | Saint Bernard . . . | — | — | 13·88 | 17·80 | 5·51 | 1·39 | 60·10 | 0·50 | 0·65 | 0·39 | ,, |
| Do. | Ancy-le-Franc . . . | — | — | 10·80 | 20·50 | 4·70 | 1·30 | 61·00 | 1·00 | 0·50 | 0·41 | ,, |
| Do. | Xeuilley . . . . . | — | — | 18·03 | 15·40 | 7·72 | 2·78 | 54·30 | 1·18 | 0·93 | 0·43 | ,, |
| Do. | Vitry . . . . . | — | — | 12·60 | 14·70 | 6·10 | 2·30 | 62·65 | 0·73 | 0·53 | 0·33 | ,, |
| Do. | Virieu (light) . . . | — | — | 10·55 | 22·40 | 5·75 | 2·70 | 56·10 | 1·50 | 1·00 | 0·50 | ,, |
| Do. | Do. (heavy) . . . | — | — | 9·50 | 26·65 | 6·50 | 2·85 | 51·80 | 1·40 | 1·30 | 0·63 | ,, |
| Do. | Argenteuil . . . . | — | — | 14·90 | 17·85 | 5·20 | 2·40 | 56·80 | 1·35 | 1·30 | 0·41 | Durand Claye |
| Do. | Les Moulineaux . . | — | — | 10·90 | 19·45 | 5·00 | 3·15 | 57·80 | 0·55 | 0·75 | 0·42 | ,, |
| Do. | Marans . . . . . | — | — | 18·20 | 13·70 | 5·90 | 2·70 | 58·10 | 1·40 | — | 0·34 | ,, |
| Italian. | Casale . . . . . | 83 | 8 days | 14·86 | 16·37 | 6·36 | | 60·48 | 0·32 | — | 0·37 | Rossi & Coen |
| Do. | Vittorio . . . . . | 50 | 18 ,, | 11·90 | 22·74 | 5·11 | | 55·20 | 2·71 | 1·37 | 0·50 | ,, |
| Do. | Palazzolo (Bergamo) . | 41 | 18 hours | 7·80 | 24·60 | 4·57 | | 60·56 | 1·72 | — | 0·48 | ,, |
| Do. | Valle Seriana (Bergamo) | 46 | 30 ,, | 9·68 | 25·00 | 6·23 | | 57·30 | 1·31 | — | 0·55 | ,, |
| Do. | Palazzolo (highly hydraulic) . . | 43 | 24 ,, | 8·37 | 25·50 | 4·48 | | 59·07 | 2·05 | — | 0·51 | ,, |
| Do. | Bellagio (Como). . . | 45 | 7 days | 24·46 | 15·48 | 4·12 | | 53·42 | 2·08 | — | 0·37 | ,, |
| Do. | Vassena (Como). . . | 50 | 36 hours | 20·84 | 13·94 | 6·28 | | 51·22 | 6·79 | — | 0·39 | ,, |
| Do. | Scandiano . . . . | 60 | 12 days | 15·21 | 18·00 | 5·68 | | 59·66 | 1·34 | — | 0·40 | ,, |

## Table VI

### Compositions of Quick-setting Cements

| Quality. | Gauging Water. | Time of Setting. | Loss on Ignition. | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | Hydraulic Index (the $Fe_2O_3$ being included with the $Al_2O_3$ where they were not determined separately). | Author. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| French. L'Albarine . . . | — | — | 8·95 | 25·45 | 9·25 | 3·85 | 47·85 | 1·45 | 0·70 | 0·72 | Durand Claye |
| Do. Argenteuil . . . | — | — | 5·30 | 29·55 | 8·35 | 4·10 | 47·50 | 3·85 | 1·35 | 0·80 | ,, |
| Do. Yonne (2 samples) | — | — | 8·35–9·60 | 20–23·40 | 8·40–12·90 | 3·30–5·70 | 47·70–52·05 | 0·95–1·05 | 2·80–3·30 | 0·55–0·76 | ,, |
| Do. Vassy (4 samples) | 40–49 | 3–14 mins. | 5·25–7·50 | 22·40–24·80 | 7–9·60 | 4·76–5·64 | 44·12–52·69 | 1·15–2·08 | 3·25–4·03 | 0·60–0·76 | Candlot |
| Do. Isère (3 samples) . | 30–33 | 5–6 ,, | 2·75–6·20 | 21·70–23·60 | 7·99–10·03 | 3·71–4·31 | 52·68–57·40 | 1·50–3·52 | 2·10–3·56 | 0·55–0·57 | ,, |
| Do. Pouilly . . . . | 37·5 | 7 ,, | 6·40 | 26·80 | 10·39 | 4·61 | 46·10 | 1·72 | 1·74 | 0·80 | ,, |
| Russian. Riga . . . . | — | — | 18·17 | 16·04 | 6·24 | 2·15 | 35·45 | 21·23 | 0·72 | 0·69 | Belelubsky |
| Do. Tchourowo . . | — | — | 14·49 | 19·47 | 7·27 | 1·48 | 36·04 | 20·08 | 1·17 | 0·78 | ,, |
| American. Rosendale . . | — | 50 mins. | 6·60 | 27·50 | 7·16 | 4·64 | 33·02 | 19·50 | 1·34 | 1·18 | Candlot |
| Do. Lehigh . . . . | — | 18 ,, | 8·90 | 24·10 | 9·12 | 3·18 | 48·24 | 2·42 | 1·64 | 0·75 | ,, |
| Austrian. Kufstein (Tyrol) | 43 | less than 15 mins. | 4·20 | 27·08 | 7·90 | 1·49 | 51·92 | 3·94 | 2·38 | 0·67 | Arlorio |
| Italian. Casale . . . . | 36 | 5 ,, | 2·13 | 24·97 | 10·72 | | 58·77 | 1·39 | 1·80 | 0·61 | Rossi & Coen |
| Do. Do. . . . | 34 | 15 ,, | 3·13 | 24·63 | 10·72 | | 59·45 | 1·20 | — | 0·59 | ,, |
| Do. Do. . . . | 42 | 8 ,, | 4·79 | 23·97 | 10·62 | | 57·80 | 1·02 | — | 0·59 | ,, |
| Do. Civitavecchia . . | 32 | 45 ,, | 2·45 | 25·94 | 13·70 | | 56·00 | 0·66 | — | 0·71 | ,, |
| Do. Palazzolo . . . | 44 | 26 ,, | 6·10 | 27·25 | 14·14 | | 46·50 | 3·67 | 2·42 | 0·89 | ,, |
| Do. Bergamo (2 samples) | 38–41 | 12–17 ,, | 3·90–4·48 | 26·12–27·90 | 12·94–18·97 | | 43·57–50·63 | 2·14–2·61 | 2·33–2·47 | 0·77–1·08 | ,, |
| Do. Vittorio. . . . | 38 | 11 ,, | 1·89 | 24·19 | 19·31 | | 42·48 | 8·68 | 2·42 | 1·02 | ,, |
| Do. Bellagio . . . | 44 | 16 ,, | 10·03 | 27·60 | 12·15 | | 43·78 | 3·83 | 1·61 | 0·91 | ,, |
| Do. Menaggio . . . | 46 | 20 ,, | 11·54 | 25·51 | 11·57 | | 43·68 | 4·07 | 2·22 | 0·85 | ,, |
| Do. Vassena . . . | 46 | 18 ,, | 10·63 | 28·69 | 12·18 | | 39·76 | 6·00 | 1·24 | 1·03 | ,, |

## TABLE VII

## Compositions of Slow-setting Cements

| Quality. | Specific Gravity. | Gauging Water. | Time of Setting. | Loss on Ignition. | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | Hydraulic Index (the $Fe_2O_3$ being included with the $Al_2O_3$, where they were not determined separately). | Author. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Portland.* | | | | | | | | | | | | |
| French (12 samples) | 3.067–3·173 | — | — | 0·40–3·40 | 21·70–25·40 | 5·20–8·33 | 2·10–3·87 | 57·42–67·31 | 0·58–2·20 | 0·26–2·23 | 0·43–0·55 | Candlot |
| English (13 samples) | 3·125 | — | — | 1·45–4·35 | 20·30–24·05 | 6·30–9·73 | 2·67–4·30 | 59·08–62·72 | 0·33–1·07 | 0·68–1·78 | 0·44–0·55 | ,, |
| German (14 samples) | 3·060–3·105 | — | — | 1·25–3·35 | 20·80–24·85 | 5·25–10·60 | 2·40–5·30 | 58·12–67·18 | 0·90–2·30 | 0·37–1·73 | 0·43–0·52 | ,, |
| Belgian (6 samples) | 3·053–3·123 | — | — | 1·20–2·95 | 23·80–26·10 | 5·33–8·51 | 2·51–3·47 | 60·03–64·12 | 0·70–0·88 | 0·74–1·54 | 0·46–0·55 | ,, |
| American (8 samples) | — | — | — | 0·45–1·86 | 20·04–23·36 | 4·86–9·74 | 1·90–4·76 | 59·95–63·34 | 0·75–4·96 | 0·52–2·00 | 0·43–0·49 | ,, |
| Russian (31 samples) | — | — | — | 0·34–4·85 | 19·20–26·63 | 3·20–8·07 | 1·82–4·52 | 61·00–64·85 | 0–2·67 | 0·16–2·26 | 0·43–0·48 | Belelubsky |
| Italian. Casale, extra. | - - | 28 | 7½ hours | 1·73 | 22·50 | 8·82 | | 64·43 | 1·25 | — | 0·49 | Rossi & Coen |
| Do. Do. I quality | — | 28 | 8 ,, | 1·80 | 22·73 | 8·64 | | 64·04 | 1·40 | — | 0·49 | ,, |
| Do. Do. II quality | — | 28 | 7 ,, | 1·45 | 23·47 | 8·59 | | 63·60 | 1·48 | — | 0·50 | ,, |
| Do. Civitavecchia | — | 29 | 5 ,, | 4·72 | 21·06 | 11·57 | | 61·67 | 0·81 | — | 0·53 | ,, |
| Do. Do. I quality | — | 27 | 12 ,, | 1·32 | 23·85 | 11·34 | | 61·44 | 1·60 | — | 0·57 | ,, |
| Do. Do. II quality | — | 28 | 8 ,, | 3·95 | 25·36 | 11·37 | | 56·03 | 1·45 | 1·49 | 0·65 | ,, |
| Do. Bergamo | — | 27 | 7½ ,, | 1·71 | 21·50 | 9·61 | | 64·38 | 1·31 | — | 0·48 | ,, |
| Do. Palazzolo | — | 27 | 7½ ,, | 4·63 | 21·45 | 9·15 | | 63·12 | 1·48 | — | 0·48 | ,, |
| Do. Vittorio | — | 29 | 7 ,, | 1·24 | 25·95 | 10·36 | | 58·81 | 2·51 | — | 0·62 | ,, |
| Do. Scandiano | — | 31 | 8½ ,, | 3·84 | 22·79 | 9·72 | | 61·82 | 1·77 | — | 0·53 | ,, |
| *Others.* | | | | | | | | | | | | |
| Natural semi-slow (Isère) | 3·012 | — | 3 hr. 10 m. | 5·10 | 22·20 | 8·32 | 3·98 | 54·40 | 2·01 | 3·60 | 0·56 | Candlot |
| Do. slow (Isère) | 3·007 | — | 6 hours | 5·10 | 21·80 | 8·32 | 4·08 | 54·10 | 3·06 | 3·70 | 0·55 | ,, |
| Mixed semi-slow (Isère) (3 samples) | 2·907–2·996 | — | 40–80 min. | 3–5·75 | 20·90–25·90 | 8·55–9·07 | 2·93–3·31 | 55–55·40 | 0·80–2·60 | 1·50–3·99 | 0·53–0·63 | ,, |
| Mixed slow (Isère) (3 samples) | 2·923–2·985 | — | 6 h. 50 m. to 7 h. 50 m. | 3·75–7·20 | 21·30–22·80 | 7·70–10·02 | 3·20–3·65 | 53·40–55·83 | 0·78–2·23 | 1·40–3·08 | 0·52–0·59 | ,, |
| Grappier's cement, French (6 samples) | 2·923–2·940 | — | 10–15 hrs. | 5–14·20 | 22·15–27·50 | 1·89–8·09 | 1·01–3·31 | 52·50–62·70 | 0·40–1·98 | 0·55–1·10 | 0·45–0·64 | ,, |
| Do. do (5 samples) | 2·814–2·935 | 35–37 | 15–24 hrs. | 4·65–6·76 | 25·70–26·71 | 3·07–4·19 | | 61·10–63·50 | 1·36–1·86 | — | 0·46–0·49 | Lab. chim. Gabelle |
| Italian cement. Palazzolo | — | 35 | 8 hours | 8·27 | 24·67 | 4·76 | | 58·38 | 1·69 | 0·54 | 0·50 | Rossi & Coen |
| Do. do. Do. | — | 35 | 9 ,, | 5·79 | 26·82 | 5·54 | | 59·18 | 2·25 | — | 0·55 | ,, |
| Do. do. Vittorio | — | 34 | 10 ,, | 4·35 | 25·75 | 4·26 | | 63·53 | 1·52 | — | 0·47 | ,, |
| Slag cement, French (8 samples) | 2·717–2·761 | — | 2–20 hrs. | 2·60–7·50 | 24·30–29·70 | 11·36–19·13 | 0·77–2·83 | 36·60–50·40 | 1·20–6·76 | 0·72–3·80 | 0·76–1·20 | Candlot |
| Do. do. Italian. Vittorio | — | 44 | 12 hrs. | 9·22 | 21·45 | 12·48 | | 50·53 | 1·89 | 0·77 | 0·67 | Rossi & Coen |

In less common use is gypsum for plastering or for slow-setting; this, having been heated at a very high temperature, has lost almost all its water. It may contain also calcium hydroxide (instead of carbonate) and calcium sulphide (from the reduction of the sulphate).

Complete examination of gypsum includes chemical analysis and various physical and mechanical tests; in practice, these are mostly reduced to the determination of the water and the setting test.

**1. Chemical Analysis.**—The water is determined by heating a weighed quantity of the sample at 160–180° to constant weight.

In general the impurities may be estimated together with sufficient accuracy by exhausting a given weight of the substance with hot water until all the calcium sulphate is dissolved and weighing the residue after drying.

When complete analysis is required, exactly 1–2 grams are dissolved in boiling, concentrated hydrochloric acid, the liquid being then diluted with boiling water, heated for a few minutes longer and filtered, and the insoluble residue ignited and weighed. In an aliquot part of the filtrate the sulphuric acid is determined by precipitation with barium chloride, and in another the alumina and ferric oxide, lime and magnesia are successively precipitated, as with limestone. If required, the carbon dioxide may also be determined.

**2. Technical Tests.**—These consist especially in determinations of the specific gravity, apparent density, fineness of grinding, amount of water required for mixing, time of setting and strength; they are made as with cements.

Properly burnt gypsum contains about 5–7·5% (on the average, 6·5%) of water and has the specific gravity 2·5–2·7 (usually about 2·68), whereas slow-setting and almost anhydrous gypsum has the specific gravity 2·7–2·95 (usually 2·93). The proportion of calcium sulphate varies from 80 to 95%. Unless present in large quantities, the impurities have no injurious influence on the hardening. Ordinary gypsum sets in a few minutes, whilst the slow-setting form takes several hours.

CHAPTER V

# METALS AND ALLOYS

This chapter contains methods for the analysis of the commoner metals and of the more important metallic alloys.

It begins with the treatment of ferrous products, descriptions being given of the principal determinations usually made on cast-iron and malleable iron; special ferrous products (special steels, ferro-metallic alloys) are then considered. Subsequently, after a short account of electrolytic analysis, the other common metals are dealt with: copper, zinc, lead, antimony, tin, nickel, aluminium, silver and gold, and their chief alloys. Lastly, methods are given for the identification of some of the metallic coatings often applied to the surface of metallic objects for purposes of embellishment or protection (gilding, silver-plating, nickel-plating, etc., and oxidation).

## IRON

Metallurgical iron products usually contain, in addition to iron, larger or smaller proportions of other elements (carbon, silicon, manganese, phosphorus, sulphur, arsenic, etc.), which exert a profound influence on the properties. Of these elements, the one of greatest interest is carbon, because, although it is not always possible to make clear and exact distinctions, it is on the carbon content and the state in which it occurs—combined or otherwise—that the distinction and classification of iron products are based.

According to the *percentage of carbon*, these products are divided into two large classes: *cast-iron* and *wrought-iron*.

The *condition* of the carbon determines the subdivision of cast-iron into *grey* and *white*, the carbon being mostly free or as *graphitic carbon* in the former and in *combination* in the latter.

A third, intermediate type, of little importance, is ***mottled cast-iron***, which is a white cast-iron containing nuclei of the grey form.

According to its *carbon content*, *malleable iron* is subdivided into *wrought-iron* and *steel*. In practice, however, the distinction between iron and steel is based, besides on the carbon content, on various other properties, such as the possibility of tempering, the strength, the microscopic structure, etc. Here, too, sharp differentiation is impossible, because the transition from one type to the other is gradual, while the presence of small proportions

of extraneous substances (tungsten, chromium, silicon, etc.) may exert a function analogous to that of carbon.

Of special technical interest are *arsenic*, *phosphorus*, *sulphur*, etc., which are almost always present in small amounts in ferrous products, and should therefore be determined, both in the crude products to decide methods of refining, and also in the refined products to ascertain if they are suitable for the required purpose.

Complete study of these products includes, then, besides exact chemical analysis, microscopical analysis and mechanical tests (resistance to tension, shock, crushing, and elasticity and torsion tests, etc.).

The chemical analysis comprises especially determinations of the *carbon* (total, graphitic and combined), *silicon*, *manganese*, *phosphorus*, *sulphur* and *arsenic*, the methods employed being described later. In rare cases, other determinations, such as those of copper, tin, antimony and oxygen, are required.

In every case, the sampling is of prime importance.

**Sampling.**—To obtain a representative sample, the whole mass of the metal should be bored with a small drill free from oil, the greatest cleanliness being observed, and the drillings caught on a sheet of brass or collected with a magnet. The whole mass should be drilled where possible, as some products, notably steels, differ appreciably in composition inside and outside.

With large ingots, samples should be taken at the two ends and the middle, at the surface and interior, and, if it is of no interest to investigate different points of the mass, a single, homogeneous sample is made of all the borings.

Small objects of wrought-iron, cast-iron or untempered steel may be sampled by means of a good steel file, cleaned with ether and benzene, the object being attacked at different points. Tempered steel must be softened by heating it in a porcelain crucible unglazed inside placed in a larger crucible of refractory material.

For very hard products, specially hard steel drills may be used. Failing this, parts of the object may be broken on an anvil with a heavy hammer and the small pieces powdered in an agate mortar, the finer material being sieved away and the coarse repowdered.

## 1. Determination of the Carbon

Carbon may occur in ferrous products in four forms:

(a) *Graphitic carbon*, consisting of fragments of graphite disseminated through the mass of the metal and insoluble in acids.

(b) *Annealing carbon*, consisting of amorphous graphite, also insoluble in acids.

(c) *Carbon combined as iron carbide*, or *carbide carbon*, soluble in hot nitric acid to a brown solution.

(d) *Hardening carbon*, contained especially in steel, and also in white cast-iron, and liberated as gaseous products during the action of hot nitric acid.

Methods are given below admitting of the determination of the total

carbon (a + b + c + d), the graphitic carbon (a + b) and the combined carbon (c + d).

**1. Determination of the Total Carbon.**—For this, numerous methods have been proposed, all based on the direct or indirect combustion of the carbon. Descriptions will be given here of the Corleis method, of the method of direct combustion in a current of oxygen (these two being most generally used) and of the copper chloride method, which requires no special apparatus and may be used in any laboratory.

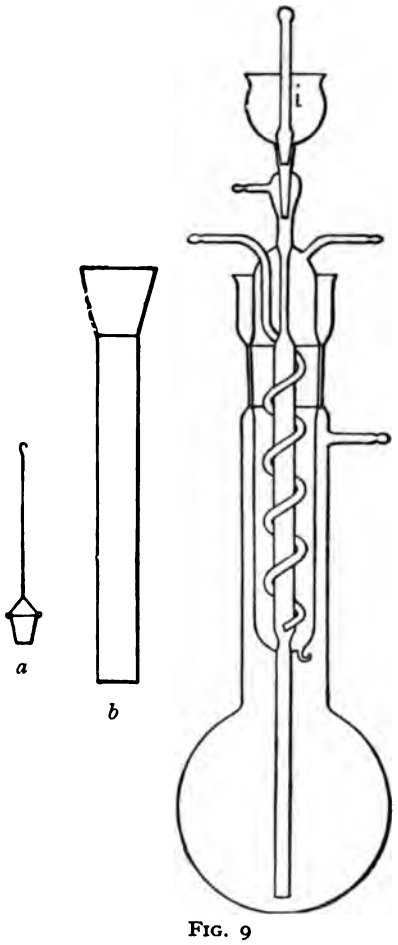

FIG. 9

(*a*) CORLEIS METHOD. This consists in treating the sample with a mixture of chromic and sulphuric acids so as to oxidise all the carbon to the dioxide, the latter being fixed and weighed.

*Reagents.* (1) *Concentrated chromic acid solution*: 720 grams of chromic acid, which need not be chemically pure but must be free from organic matter (the pure chromic acid of commerce), are dissolved in 700 c.c. of water.

(2) *Copper sulphate solution*: 400 grams of crystallised copper sulphate are dissolved to 2 litres.

*Apparatus.* The necessary apparatus is shown in Fig. 10 on p. 165,[1] and includes:

(1) A tower *A* to purify the air and containing potassium hydroxide solution at the bottom and soda lime or lump potash in the upper part.

(2) The Corleis flask, modified to some extent, consisting of a 700–900 c.c. flask (shown in detail in Fig. 9) fitted with a small ground-in condenser which descends inside the neck, and the mouth of which is hollowed to the form of a small basin to hold sulphuric acid to seal the ground-in plug; by means of two tubes a current of air may be passed through the flask.[2]

(3) A drying flask *C*, charged with sulphuric acid to about 3 mm. below the end of the gas tube.

[1] This figure and many of the others shown were designed by Dr. B. Gasparinetti.

[2] To prevent breaking of the flask during heating it is well to wrap the bottom in asbestos. A disc of asbestos board about 0·5 mm. in thickness is prepared and a number of radial slits made almost to the centre; the disc is then moistened and stuck to the bottom of the flask. After drying in the oven the asbestos remains perfectly adherent to the vessel.

(4) A small glass or glazed porcelain combustion tube *D*, filled with copper oxide and heated by two or three bunsen fan flames, with the object of transforming into carbon dioxide the small amounts of carbon monoxide or hydrocarbons which may be formed in the reaction.

(5) A U-tube (*E*) with ground stoppers and filled with phosphoric anhydride to retain the moisture in the gas.[1]

(6) Two U-tubes (*F*, *F*), with ground stoppers, for absorbing the carbon dioxide; the left branch and half of the right are charged with granular soda lime (granules 1–1·5 mm.) covered with loose glass wool plugs, the rest of the right limb being filled with phosphoric anhydride also capped with a glass wool plug. One of these tubes is usually sufficient to fix all the carbon dioxide evolved, and may be used for several determinations, the other serving as control.[2]

(7) A U-tube (*G*) containing phosphoric anhydride and a wash-bottle (*H*) with conc. caustic soda solution to protect the absorption tubes from atmospheric moisture and carbon dioxide.

(8) An aspirator (*I*) to regulate the gas current.

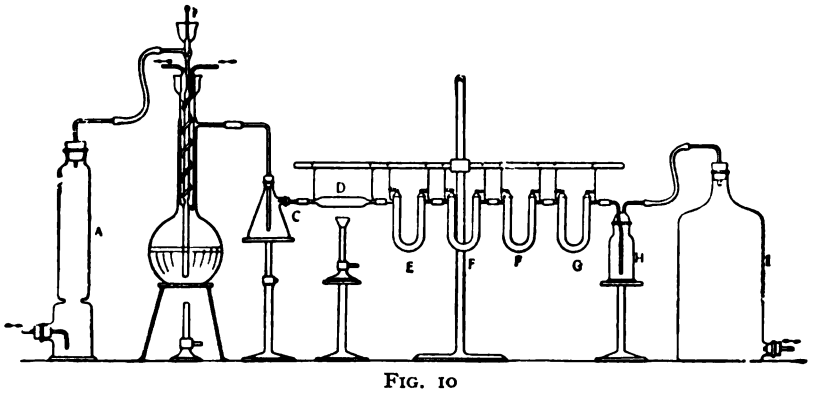


FIG. 10

*Procedure.* When the apparatus has been fitted together as shown and the joints made air-tight, 35 c.c. of the chromic acid solution, 150 c.c. of the copper sulphate solution and 200 c.c. of conc. sulphuric acid (D 1·84) are introduced into the flask by raising the ground glass plug of the funnel *i*; to destroy any organic matter present, the mixture is boiled for about half an hour, a gentle current of air being drawn through the apparatus and the glass or porcelain tube heated. During this preliminary operation it is useless to insert the series of U-tubes.

Meanwhile the soda lime tubes are weighed and also the sample, which should be in powder or fine filings.[3]

[1] The phosphoric anhydride may be replaced by calcium chloride, provided that this has been recently saturated with carbon dioxide to neutralise alkalinity due to the presence of lime.

[2] These two tubes may be replaced by Geissler bulbs filled with 30% caustic potash solution.

[3] The sample may be weighed either in a small glass tube with a foot and poured into the flask through a funnel (Fig. 9, *b*) with a long, wide stem, or in a small platinum bucket which is suspended in the liquid in the flask by a platinum wire attached to a suitable hook fused on to the bottom of the condenser (Fig. 9, *a*), or in a small thin-walled glass tube which is introduced directly into the flask.

With pig iron containing 3-4% of carbon, 1 gram is taken; with steel containing more than 0·3%, 3 grams, and with soft iron containing less than 0·3%, 5 grams.

When the liquid in the flask is quite cold the absorption bulbs are fitted, a little sulphuric acid is placed in the funnel *i*, the condenser is raised and the weighed metal introduced into the flask, the condenser being then rapidly replaced and a little sulphuric acid poured into the annular cavity to ensure perfect fitting.

The burners under the combustion tube are then lighted and a moderate current of air (2–3 bubbles per second) passed through the apparatus, while the flask is heated carefully so as to bring the liquid to boiling in 10–15 minutes. Boiling should be continued for about 3 hours, the flow of gas being kept regular and the flame being lowered or removed immediately if pressure develops in the flask and tends to drive the liquid along the tube used for the introduction of the acid.

Towards the end the air-current is accelerated a little to displace all the carbon dioxide from the apparatus, the absorption apparatus being afterwards closed, the flames extinguished and the weighings made. The total carbon in the sample is obtained by multiplying the carbonic anhydride found by 0·27273.

To ascertain if the sample has been acted on completely, the cold mixture of sulphuric and chromic acids is diluted with a large amount of water in a large beaker and, after a short time, the deposit collecting at the bottom of the beaker is tested for iron particles by means of a magnet brought near to the outside.

The Corleis method is usually adopted for the analysis of iron, cast-iron and steel, but is unsuitable with products difficult of attack by sulphuric-chromic acid mixture, such as ferro-silicon, ferro-chromium, ferro-tungsten, etc. For the latter, the direct combustion method should be used (*see* later).

Corleis observed that, in the determination of the carbon in steels under the above conditions, only 2% of the total carbon is liberated as hydrocarbons, so that the apparatus may be simplified by the suppression of the combustion tube, the result then obtained being increased by 2%.

(*b*) Direct Combustion in a Current of Oxygen. This method consists in heating the sample at 1050–1150° in a current of oxygen and absorbing the carbon dioxide thus formed in the usual way.

*Apparatus*: (1) Gasometer containing oxygen.

(2) Wash bottles containing sodium hydroxide solution and conc. sulphuric acid respectively, and a small U-tube with calcium chloride.

(3) A quartz or externally glazed porcelain combustion tube (50–60 cm. long, 1·5 cm. bore), closed by rubber stoppers protected from the heat by asbestos board and containing, at the end near the absorption apparatus, a short layer of cupric oxide to oxidise any carbon monoxide which may be formed.

(4) An electric resistance furnace for heating the tube, with rheostat and amperemeter (*see* Fig. 11).

(5) A Le Chatelier thermo-electric couple of platinum and platinum-

rhodium wires with corresponding galvanometer-pyrometer (Fig. 11, *P*, *G*).

(6) Two U-tubes, one filled with pumice and chromic acid and the other with calcium chloride and phosphoric anhydride.

(7) The usual absorption apparatus for the carbon dioxide (*see* preceding method), followed by a sulphuric acid wash-bottle.

*Procedure.* When the apparatus is arranged, a moderate current of oxygen is passed for about 10 minutes and then, complete elimination of the air being ensured, without interrupting the flow of gas the absorption apparatus is detached and weighed when it has reached the temperature of the surrounding air.

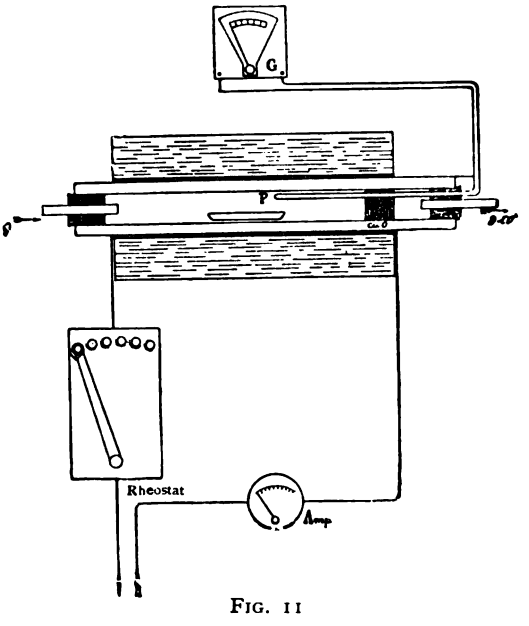


FIG. 11

Meanwhile the furnace is heated and the sample weighed in an unglazed porcelain boat (10–12 cm. long, 1·4 cm. wide). Of malleable iron or ordinary cast-iron, 1 gram is taken, or of iron alloys rich in carbon, such as ferro-manganese, ferro-chromium, etc., 0·5 gram. The sample should not be too finely powdered in order that too violent combustion may be avoided.

When the furnace reaches a temperature of about 900°, the stream of oxygen is interrupted and the boat pushed exactly into the middle of the tube by means of a copper wire or a quartz rod fitted with a hook, the tube being then quickly closed and the absorption apparatus attached.

A fairly rapid current of oxygen is then passed and the temperature of the furnace raised to between 1050° and 1150° in 15–20 minutes. The latter temperature should not be exceeded, since otherwise the furnace may be damaged and the sample may begin to fuse and enclose a little carbon, which may thus escape complete combustion. The temperature is kept at 1050–1150° for 15–20 minutes, the heating being then interrupted and the velocity of the oxygen increased until about 700° is reached, when the absorption apparatus is detached and, 15–20 minutes later, weighed. The weight of the carbon dioxide, multiplied by 0·27273, gives the carbon in the sample taken. After removal of the boat the apparatus is ready for the next determination.

In determining carbon in certain ferro-metallic alloys, such as ferro-silicon, ferro-chromium and ferro-manganese, it is necessary to add a catalyst to ensure the complete oxidation of the carbon. According to Ledebur, the best results are obtained by cobalt oxide, which should be calcined for half an hour in an electric furnace at about 1000° before use. One gram of the oxide is mixed in

an agate mortar with 0·5 gram of ferro-chromium or ferro-manganese, or 1–2 grams of the oxide with 1 gram of ferro-silicon, the mixture being introduced quantitatively into the boat and the combustion carried out for 1½–2 hours at 1050°.

With readily fusible ferro-metallic alloys, such as ferro-vanadium and ferro-molybdenum, it is advisable to mix with a little refractory clay.

The above method of estimating the total carbon, which is coming more and more into general use, combines exactness with great rapidity (for ordinary products, 30–40 minutes suffice) and has the great advantage over the Corleis method that it is applicable to any ferrous product.

(*c*) COPPER CHLORIDE METHOD. This method consists in attacking the iron with a reagent, such as copper-potassium chloride, which leaves the carbon unchanged, and in determining the carbon separated by combustion. It is less exact but simpler than the two preceding methods and may always be used with advantage for products rich in carbon.

Such quantity of the finely powdered sample is taken as will liberate about 0·015–0·02 gram of carbon: 3 grams of steel containing about 0·5% of carbon, 1 gram of cast iron with not much more than 2% of carbon, and 0·5 gram of products still richer in carbon.

An aqueous 30% solution of copper-potassium chloride is prepared as free as possible from organic matter, 50 c.c. of this solution being used per gram of metal to be attacked.

This volume of the solution is placed in a 250 c.c. conical flask and acidified with a little hydrochloric acid to prevent the dissolution of small quantities of carbonaceous matter, the weighed sample being then added and the flask shaken. The iron passes immediately into solution liberating copper, which, however, dissolves completely in the excess of the reagent on gentle heating and shaking, leaving a black residue containing the whole of the carbon. The action is usually complete in about half an hour.

Any basic iron salt formed is then dissolved by addition of a few drops of hydrochloric acid and the liquid filtered through a Gooch crucible containing ignited asbestos. If all the carbon is retained by the filter, dilution of a few drops of the brown filtrate with water acidified with hydrochloric acid yields a clear, greenish solution. The flask and residue are washed first with dilute copper-potassium chloride solution acidified with hydrochloric acid and then with distilled water until the wash water no longer contains chloride, the crucible being then dried at a low temperature.

The asbestos with the carbon are then burnt in a platinum boat in a combustion tube through which oxygen is passed, the procedure being that followed in ordinary elementary analysis of organic compounds. Between the combustion tube and the absorption bulbs for the carbon dioxide (Geissler bulbs), two U-tubes are inserted, one with pumice soaked in sulphuric acid saturated with chromic acid to oxidise and retain any sulphur dioxide formed by oxidation of sulphur or sulphides, and the other copper sulphate dehydrated at 200° to catch moisture and any traces of hydrochloric acid. $CO_2 \times 0{\cdot}27273 =$ carbon.

For the combustion of the carbonaceous residue separated, the above method may be replaced by treatment with chromic and sulphuric acids in the Corleis apparatus (*see* p. 164). Certain products, such as ferro-silicon, ferro-chromium,

ferro-tungsten, etc., are not completely attacked by copper-potassium chloride, and cannot, therefore, be analysed in this way (*see* p. 168).

**2. Determination of the Graphitic Carbon** (graphitic carbon and annealing carbon).—These are not altered by hot dilute nitric acid, whilst the combined carbon (hardening carbon and carbide carbon) are converted into volatile or soluble products. On this difference is based the method of separation of the two types of carbon.

As a rule, 1 gram of grey cast-iron or 2–3 grams of white cast-iron or 5–10 grams of steel, are treated in a tall, narrow beaker covered with a watch glass with nitric acid of D 1·2 (about 25 c.c. per gram of metal), the beaker being cooled at first to prevent an excessively violent reaction. When the reaction begins to slacken, the beaker is heated on a sand-bath to complete the action and, if much silicon is present, when the metal is entirely attacked 0·5–1 c.c. of pure hydrofluoric acid is added from a platinum crucible without touching the sides of the beaker.

The liquid is gently boiled for 1–1½ hour and is then diluted with water, the insoluble matter being allowed to settle and collected on a Gooch crucible and washed with hot water until free from acid.

After being dried at not too high a temperature, the asbestos and graphitic residue are oxidised either in the Corleis apparatus with chromic and sulphuric acids (*see* p. 164) or in an open tube in a current of oxygen (*see* p. 167).

According to Ledebur, the graphitic carbon separated may be collected and weighed directly on a filter dried at 100° and tared. To ensure complete removal of extraneous substances, the residue should be washed twice with hot water, twice with hot 5% caustic potash solution, twice with hot water, twice with hot, dilute hydrochloric acid (1 : 3), and finally three times with hot water. In this case the addition of hydrofluoric acid to eliminate every trace of silicon is, of course, indispensable.

**3. Determination of the Combined Carbon** (carbide carbon and hardening carbon).—The combined carbon in cast-iron may be calculated as the difference between the total carbon and the graphitic carbon determined by the methods already given.

In malleable iron and especially in steel, which do not contain graphitic carbon, the determination of the combined carbon (in this case, the total) may be carried out by the rapid colorimetric method.

Colorimetric Determination of the Combined Carbon (Eggertz method). This is based on the fact that hot nitric acid leaves the graphitic carbon unaltered, while the combined carbon is partly liberated as gas (hardening carbon) and partly dissolved in the acid (carbide carbon), which is coloured a more or less intense brownish-red in dependence on the quantity of carbon.

In general, the proportions of carbide carbon and hardening carbon in untempered steels [1] are in almost constant ratio, so that, if parallel tests are made on the sample under examination and on a steel with a known content of carbon, the solutions obtained will have colour intensities proportional, not only to the content of carbide carbon but to the content of total combined carbon.

[1] This method is consequently inapplicable to tempered steels.

*Procedure.* Of the finely powdered steel and of a typical steel, 0·1 gram is introduced into each of two thick-walled test-tubes (123 mm. high and 15 mm. in diam.). Into each tube 5 c.c. of nitric acid (D 1·18–1·2) *free from hydrochloric acid* are poured, the tube being covered with a funnel and immersed in a bath of cold water to allay the vigour of the reaction. After a short time the tubes are transferred to a vessel of water and heated at 80–100° [1] for 1–2 hours, care being taken that the level of liquid in the bath is not more than about 1 cm. higher than that in the tubes.

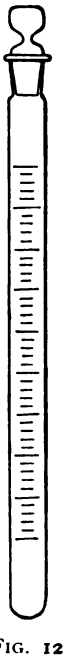

FIG. 12

After 1–2 hours' heating, when the action is at an end, the tubes are cooled in cold water and the solutions poured into white glass tubes of the same bore and thickness, holding 30 cm. and divided into tenths of 1 c.c. (Eggertz tubes, *see* Fig. 12), filtering if necessary (that is, if much silica remains) through a small asbestos filter away from direct light

To carry out the colorimetric comparison the volume of each solution is made up to 8 c.c., in order that the colour may not be influenced by that of the dissolved iron or impurities and the colours viewed by transmitted and reflected light. The darker one is then carefully diluted with water until the intensities correspond; the tubes should be interchanged and the comparison repeated.

The comparison is facilitated by the use of a box with opaque, black, lateral walls, the back one sliding up to admit of examination by transmitted light. The combined carbon is deduced from the proportion,

$$V : v = C : x,$$

where $V$ and $v$ are the respective volumes of solution from the control steel and the steel under examination and $C$ and $x$ the corresponding contents of combined carbon.

With practice the *colorimetric* method gives sufficiently exact results and is rapid and permits of several simultaneous determinations. It is naturally of advantage to compare steels of the same kind, e.g., a Martin steel with another Martin steel and a Bessemer steel with a Bessemer steel, and the control steel—the carbon-content of which should be determined very accurately by combustion—should have about the same content of carbon as, or better a rather greater content than, the steel to be examined. In general it is sufficient to have a series of control steels containing approximately: 0·06, 0·12, 0·15, 0·20, 0·30, 0·50, 0·80 and 1·20% of carbon. If the steel has a carbon-content greater than 0·8%, the calculation may be simplified by diluting the solution of the control steel to such a volume that the number expressing the c.c. corresponds with the carbon-content of the steel (the solution of a control steel containing, say, 0·9% of carbon would be diluted to 9 c.c.). When the solution from the steel to be tested has the same colour as that from the control steel, its volume divided by 10 gives at once the percentage of carbon.

The *colorimetric* method cannot be used for steels containing metals capable of modifying appreciably the coloration of the nitric acid solution, such as chromium, copper, nickel, etc.

[1] The temperature is easily maintained at 80–100° by placing the bath containing the tubes on a boiling water-bath.

## 2. Determination of the Silicon

When wrought-iron, cast-iron and steels are dissolved in mineral acids, the silicon present separates, after evaporation, as silica which may be collected and weighed. In practice, the metal is treated sometimes with hydrochloric and sometimes with nitric acid (in some cases sulphuric and nitric acids together), according to the operations to be carried out subsequently on the liquid. Thus, if only the silicon is to be determined or if the liquid is to be used for estimations not affected by the presence of hydrochloric acid, the latter is preferred owing to its more rapid action. In some cases, however, the next estimation to be made with the liquid—e.g., that of phosphorus—renders necessary the use of nitric acid. Both methods of acting on the metal are in common use and will be described.[1]

**1. Attack of the Metal with Hydrochloric Acid.**—In a porcelain dish covered with a clock-glass 2–4 grams of the sample [2] are heated with hydrochloric acid of D 1·12 (about 10 c.c. per gram of metal) on the water-bath until the iron is completely dissolved. The clock-glass is then removed and washed into the basin and the liquid evaporated to dryness on the water-bath, care being taken to mix with a platinum spatula the mass of ferric chloride separating; the residue is then heated for an hour in an oven at 135°.

When cold, the dish is again covered with a clock-glass and the residue moistened with 10 c.c. of hydrochloric acid (D 1·12), heated for some time on the steam-bath, diluted with 100–150 c.c. of hot water, mixed and, after cooling, filtered, the residue being washed with cold water acidified with hydrochloric acid until the wash water is free from iron. At this point a few drops of hydrochloric acid (D 1·12) are allowed to flow down the edge of the filter, which is again washed with cold distilled water.

The moist filter is placed point upwards in a tared platinum crucible and carefully burnt, the crucible being ignited for 4–5 minutes in the blow-pipe flame and, when cold, weighed.

The silica thus separated may contain various impurities, such as graphitic carbon, traces of ferric oxide, tungsten oxide, titanic acid, etc.

To determine the true silica content, the weighed residue is treated in the crucible with 1–2 c.c. of water, 1–2 drops of conc. sulphuric acid and 5–6 c.c. of hydrofluoric acid (puriss.). Evaporation is then carried as far as possible on the steam-bath and the slight excess of sulphuric acid expelled by heating the inclined crucible over a small flame. When evolution of sulphuric acid vapour ceases, the crucible is heated to redness and weighed when cold. The loss in weight gives the silica and this, multiplied by 0·4693, the silicon.

It sometimes happens, especially with cast-iron rich in graphite, that the silica separated is grey. In this case, the treatment with hydrofluoric acid is omitted and the contents of the crucible heated to gentle fusion with a little sodium carbonate and potassium nitrate. When cold, the mass

[1] For the determination of silicon in products insoluble in acid, *see* Ferro-silicon.

[2] With samples containing little silicon, such as ordinary carbon steels, 5–10 grams are taken.

is dissolved in water and the solution transferred to a porcelain dish and acidified with hydrochloric acid. After evaporation to dryness on a steam-bath, the residue is moistened with hydrochloric acid and again evaporated, heated in an oven at 135°, taken up with hydrochloric acid, diluted, heated and, after cooling, filtered ; the silica is subsequently washed, dried, ignited in a platinum crucible and weighed.

**2. Attack of the Metal with Nitric Acid.**—With grey cast-iron or silicon steel (3-5% Si), 2-4 grains, or with white cast-iron or ordinary steel, 5-10 grams, of the sample are introduced into a thin porcelain dish 12–15 cm. in diameter. The dish is covered with a clock-glass and dilute nitric acid (D 1·18) gradually added, addition of fresh acid being made only when the initial vigorous action begins to slacken. Each gram of metal requires about 12 c.c. of acid.

When the required amount of acid has been added, the dish is heated on a steam-bath to complete the action [1] ; the clock-glass is then removed and washed and the liquid evaporated on a steam-bath, the dish being frequently shaken to break the skin forming on the surface, and towards the end of the operation the liquid stirred with a platinum spatula to prevent spurting. When dry, the residue is heated further on a sand-bath or asbestos until a powdery residue remains ; the heat is then gradually increased to redness, which is maintained until the nitrates are completely decomposed, i.e., until evolution of brown vapours ceases.

The cold residue is moistened with conc. hydrochloric acid and heated for a short time, a further addition of 9–10 c.c. of conc. hydrochloric acid per gram of metal dissolved being made and the liquid heated and stirred until the ferric oxide is completely dissolved. To ensure that the silica becomes absolutely insoluble, the hydrochloric acid solution is evaporated to dryness and the residue heated for an hour in an oven at 135°.

The residue is taken up again in conc. hydrochloric acid (5–6 c.c. of acid per gram of metal), heated, diluted and, when cold, filtered, the silica being purified in the same way as when the metal is attacked with hydrochloric acid (*see* p. 171).

The filtrate may be used for the determination of phosphorus (*see* p. 173).

## 3. Determination of Manganese

Manganese, which is always present in larger or smaller amount in iron, cast-iron or steel, may be estimated gravimetrically, volumetrically or colorimetrically. The volumetric method will be described later (*see* Ferro-manganese) and here will be given only the colorimetric method, which, owing to its rapidity, is the most commonly used for determining the small proportions of manganese contained in iron and in ordinary steels.

**Colorimetric Determination of Manganese** (according to Ledebur). —This method consists in acting on the sample with nitric acid, oxidising

[1] The more or less intensely brown liquid should, however, be clear ; if it appears turbid, a little more acid should be added.

the manganese to permanganic acid and comparing the colour of the solution with that of a permanganate solution of known titre.[1]

*Preparation of the control solution*[2]*:* 0·072 gram of chemically pure potassium permanganate is dissolved in water and the volume made up exactly to 500 c.c.; 1 c.c. of this solution corresponds with 0·05 m. grm. of manganese.

*Procedure.* 0·2 gram of the metal is dissolved in the hot in 15–20 c.c. of nitric acid (D 1·2) in a 100 c.c. measuring flask, the liquid being afterwards heated to boiling to expel nitrous fumes, cooled, made up to volume and mixed.

Four portions, each of 10 c.c., are pipetted into four beakers of about 75 c.c. capacity, 2 c.c. of nitric acid (D 1·2) being added to each beaker. The first portion is heated over a small flame to boiling, the beaker being covered with a clock-glass meanwhile. The cover is then quickly removed, about 0·5 gram of lead peroxide free from manganese added to the boiling liquid and gentle boiling maintained for two minutes longer.

When cold, the liquid is filtered by decantation—care being taken that no lead peroxide passes—through a small asbestos (this being ignited, and washed with permanganate solution and then with water) filter, the filtrate being collected in an Eggertz tube (*see* Fig. 12, p. 170) and the residual lead peroxide and the filter washed with about 5 c.c. of water until the wash water passes through colourless. The solution in the Eggertz tube, when shaken, is ready for the colorimetric observation.

The other three portions are treated in the same way, the filtrations being effected with the same filter and the liquids collected in Eggertz tubes to serve for confirmatory purposes.

The colorimetric comparison is made by pipetting into another Eggertz tube 1–4 c.c. of the control permanganate solution according to the colour intensity of the other tubes, and diluting carefully with water until an exact match is obtained.

If the volume of the solution from the sample of steel is $v$ and 1 c.c. of the control solution has to be diluted to $V$ c.c. to give the same depth of colour, the percentage of manganese in the sample will be

$$x = \frac{v \times 0{\cdot}05}{V} \times 5.$$

This rapid and fairly accurate method cannot be applied to materials containing more than 1–1·5% of manganese.

## 4. Determination of the Phosphorus

Many methods are in use for the determination of phosphorus in ferrous products, those most generally employed being based on the conversion of the phosphorus into phosphoric acid and precipitation of the latter with ammonium molybdate. The ammonium phosphomolybdate separated may be determined gravimetrically, volumetrically, densimetrically, etc. Descriptions will be given here of Finkener's gravimetric method, which

[1] Some prefer to make the comparison with a steel of known manganese content.
[2] This solution, stored in the dark, keeps for about three weeks.

is considered the most exact, and the rapid method of weighing the ammonium phosphomolybdate directly, with references to the modifications necessitated in both methods by the presence of arsenic, vanadium and tungsten.[1]

**1. Gravimetric Determination of Phosphorus in absence of Arsenic, Vanadium and Tungsten.**

(*a*) FINKENER'S METHOD. *Reagents:* (1) Ammonium molybdate solution, prepared by dissolving 80 grams of powdered ammonium molybdate in a mixture of 640 c.c. of water and 160 c.c. of 20% ammonia (D = 0·925) and pouring this solution into a cold mixture of 960 c.c. of 30% nitric acid (D = 1·18) and 240 c.c. of water. This reagent should be left at rest for some days in the dark.

(2) Washing liquid, prepared by dissolving 150 grams of ammonium nitrate in water, adding 10 c.c. of conc. nitric acid and diluting to 1 litre.

*Procedure.* 5 grams of slightly phosphoric iron or steel, or 1–2 grams of cast-iron, or 0·5–1 gram of material very rich in phosphorus, are treated in a porcelain dish with nitric acid of D = 1·2 (about 12 c.c. per gram of metal), the liquid being evaporated to dryness and the residue ignited and treated with hydrochloric acid and the silica removed and determine if required as in the estimation of silicon by the nitric acid method (*see* p. 172).

The hydrochloric acid solution is evaporated to a syrup in a 250 c.c. beaker, this allowed to cool (no basic iron salt should separate on cooling) and 50–100 c.c. of the molybdic reagent (according to the amount of phosphorus present) stirred in by means of a rod to facilitate the separation of the precipitate. After a stand of about half an hour in the cold, chemically pure solid ammonium nitrate is added to the extent of about 25% of the liquid, the salt being dissolved by stirring.

After 18–24 hours at the ordinary temperature, the clear supernatant liquid is filtered by decantation, the filtrate being collected in a 300 c.c. conical flask, the beaker and precipitate washed with the washing liquid mentioned above until the latter no longer gives the reaction for iron, and the precipitate then transferred to the filter.[2]

A few c.c. of hot dilute ammonia solution are then poured into the beaker to dissolve the small quantity of adherent precipitate and, a porcelain crucible of 30–45 c.c. capacity—tared with the lid—having been placed under the funnel, the ammoniacal solution is poured carefully on to the filter, the precipitate rapidly dissolving. The beaker and filter are washed with faintly ammoniacal water and the solution evaporated on a water-bath to expel the ammonia, the volume being reduced to 8-10 c.c.; 4–5 drops of conc. nitric acid are then added to bring about the re-formation of ammonium phosphomolybdate and the solution evaporated to dryness.

The crucible is next heated in an ordinary air-oven or, better, a Finkener

[1] For the determination of phosphorus in products unattacked by acids, *see* Ferro-silicon.

[2] When the precipitate is transferred to the filter, it is well to replace the 300 c.c. flask by a smaller one in order that less liquid will require filtering should the filtrate *pass* through turbid.

oven, to eliminate the ammonium nitrate, the temperature being raised gradually to 160–180°; excessive heating must, however, be avoided as it entails the danger of reducing the molybdic acid. If a dry, cold watch-glass placed on the crucible does not become dimmed in about half a minute, the expulsion of the ammonium salts is complete and the hot crucible is allowed to cool in a desiccator and weighed as rapidly as possible to prevent absorption of moisture. (Ammonium phosphomolybdate) × 0·0164 = phosphorus.

As already mentioned, phosphorus may be determined directly in the liquid from which the silica has been filtered, in the case when the metal was dissolved in nitric acid. In this case the hydrochloric acid solution freed from silica is evaporated to a syrup in a 250 c.c. beaker, allowed to cool (no basic iron salt should separate) and 50–100 c.c. of molybdate reagent added according to the quantity of phosphorus present, the remaining procedure being as above. When a large amount of substance has been taken for the silicon estimation, the phosphorus determination is made on an aliquot part of the filtrate.

Further, if a very large amount of phosphomolybdate separates, some prefer to dissolve it in ammonia and filter, and precipitate by means of magnesia mixture. In this case, the magnesium ammonium phosphate is collected on a filter after 6–7 hours, and washed with slightly ammoniacal water until the washings pass through free from chlorine, the paper precipitate being incinerated together at not too high a temperature and then strongly ignited to constant weight in a blowpipe flame: $Mg_2P_2O_7 \times 0{\cdot}2787 = P$.

(*b*) Direct Weighing of the Ammonium Phosphomolybdate (Rapid method).—5 grams of iron or steel of low phosphorus content, or 1–2 grams of cast-iron, or 0·5–1 gram of material rich in phosphorus, are heated in a conical flask with nitric acid of D = 1·2 (about 12 c.c. of acid per gram of metal) and the solution treated with 1–2 c.c. of hydrofluoric acid [1] to eliminate the silica and then heated for a few minutes longer.[2] To oxidise the phosphorus completely, 5–10 c.c. of 2% permanganate solution are added with shaking and the heating continued for 2–3 minutes, 3–4 c.c. of 25% potassium oxalate being then added and the liquid heated until the separated manganese dioxide completely dissolves. Ammonia is next added, drop by drop, to the clear solution until the first flocks of ferric hydroxide separate, these being dissolved by a few drops of nitric acid. The liquid is then transferred to a beaker and evaporated to a syrup, allowed to cool to 50° and treated with 50–100 c.c. of ammonium molybdate solution previously heated to 50°, and, after some time, 15–20 grams of solid ammonium nitrate, which is dissolved by shaking. After the beaker has been left for about an hour at 45–50°, the phosphomolybdate precipitate is collected on a tared Gooch crucible containing asbestos which has been previously ignited and washed with nitric acid and then with water. The precipitate is washed with water acidified with 1% of nitric acid of D = 1·2 until the liquid passing through is free from iron and is then heated in an

[1] The hydrofluoric acid is poured in from a platinum dish or crucible in such a way that it does not come into contact with the walls of the flask.

[2] If the sample contains much graphitic carbon the solution, after treatment with hydrofluoric acid, is made up to a definite volume and filtered through a dry filter, an aliquot part being taken, treated with permanganate, and so on.

oven at 70-80° to constant weight.[1] Phosphomolybdate × 0·0164 = phosphorus.

**2. Determination of the Phosphorus in presence of Arsenic.**—If not more than 0·1% of arsenic is present, the methods described above give accurate results, but with larger proportions of arsenic, the latter must be eliminated from the phosphorus precipitate. After the metal has been acted on, the silica removed, etc., as before, the hydrochloric acid solution is treated in a roomy dish, gradually and with stirring, with 10–20 c.c. of pure hydrobromic acid[2] of D = 1·49 (containing about 48% of hydrobromic acid) and evaporated to dryness on a water-bath. The arsenic is thus volatilised, probably as the tribromide, whilst all the phosphorus remains. The residue is taken up in dilute hydrochloric acid, the solution evaporated in a 250 c.c. beaker to a syrup, and the phosphoric acid precipitated as usual.

**3. Determination of Phosphorus in presence of Vanadium.**—In presence of vanadium, the ammonium phosphomolybdate, which is then orange-coloured, is dissolved in dilute ammonia and the solution evaporated to 20 c.c., a few drops of dilute ammonia being added from time to time. The cooled-slightly ammoniacal liquid is then saturated with ammonium chloride (5–6 grams are added), care being taken that undissolved crystals remain in the solution. The vanadium is thus precipitated as ammonium metavanadate which, after 6–10 hours, is filtered and washed with ammonium chloride solution (250 grams per litre) until the washings no longer give the phosphate reaction with molybdate, the phosphate being then precipitated in the filtrate by means of magnesia mixture.

**4. Determination of Phosphorus in presence of Tungsten.**—In this case the phosphomolybdate precipitate is dissolved in ammonia and the phosphate precipitated with magnesia mixture (*see* p. 175).

## 5. Determination of the Sulphur

Of the various methods proposed, the gravimetric and volumetric methods will be given here.

**1. Gravimetric Determination.**—(*a*) M. Arnold's method[3]: 6 grams of the sample are mixed with 1 gram of potassium chlorate and treated in a porcelain dish covered with a clock-glass with 50 c.c. of conc. nitric acid containing in solution 1 c.c. of bromine. When evolution of gas ceases, 10 c.c. of hydrochloric acid are added and the liquid evaporated to dryness on a sand-bath and the residue heated in an oven at 105° for 5-6 hours. The residue is then taken up in 30 c.c. of hydrochloric acid, the liquid evaporated to 10 c.c., diluted with water and the solution poured into a 60 c.c. measuring flask, made up to volume and filtered through a dry pleated filter.

Of the filtrate, 50 c.c. (corresponding with 5 grams of the sample) are

[1] The slight reduction of the phosphomolybdate observable round the walls of the crucible has scarcely any influence on the accuracy of the result.

[2] The freedom of this acid from phosphorus must be ascertained by a blank test.

[3] For acting on the metal, Campredon's modification is followed.

treated in a beaker in the cold with 20 c.c. of 10% barium chloride solution. The volume is made up to about 100 c.c. with water, the liquid stirred and, after standing for 12–24 hours, filtered by decantation and the precipitate finally transferred to the filter and washed alternately with hot dilute hydrochloric acid (10%) and cold water until the washings no longer give the iron reaction with thiocyanate. The barium sulphate thus obtained, which should be perfectly white, is dried, ignited and weighed: $BaSO_4 \times 0{\cdot}1374 = S$ (in 5 grams of sample).

This method is moderately delicate. In presence of large quantities of iron the precipitation may sometimes be incomplete or the barium sulphate may contain iron as an impurity. This difficulty is obviated by Meinecke [1] and by Carnot and Goutal [2] by the following method (*see b*), the iron being removed by means of copper-potassium chloride, and the oxidation of the sulphur being made on the insoluble residue, which contains the sulphur as sulphides of copper and iron and only very little of the latter.

(*b*) MEINECKE, CARNOT AND GOUTAL'S METHOD. 5 grams of the finely powdered sample are heated, with frequent shaking, with about 50 grams of copper-potassium chloride and 250 c.c. of water (*see* Determination of carbon by means of copper chloride) for about 15 minutes on a water-bath, 10 c.c. of hydrochloric acid being then added and the liquid again heated to dissolve the separated metallic copper. The insoluble residue is then collected on a small paper or asbestos filter and washed with hot water. The filter and precipitate are then evaporated on a water-bath to dryness in a small dish with a little potassium chlorate, 5 c.c. of nitric acid (D 1·4) and 10 c.c. of hydrochloric acid (D 1·19). The residue is then taken up with a little hydrochloric acid, again heated almost to dryness on a water-bath, diluted, and filtered and washed with hot water. The filtrate is neutralised with ammonia, acidified slightly with hydrochloric acid and precipitated in the hot with barium chloride.

This method is sufficiently exact and rapid.

**2. Volumetric Determination of the Sulphur** (Rollet & Campredon's method).—When wrought-iron, cast-iron or steel is acted on by hydrochloric or sulphuric acid, the sulphur present is liberated mostly as hydrogen sulphide and in small part as sulphur compounds [especially $(CH_3)_2S$], which may be reduced to hydrogen sulphide by heating in presence of hydrogen in a porcelain tube. The hydrogen sulphide is fixed by zinc acetate and the sulphide formed determined iodometrically.

*Reagents:* (1) 25 grams of pure, crystallised zinc acetate and 1 c.c. of acetic acid dissolved to 1 litre.

(2) 7·928 grams of resublimed iodine are dissolved with the help of 25 grams of potassium iodide and the volume made up to 1 litre: [3] 1 c.c. corresponds with 0·001 gram of sulphur.[4]

[1] *Zeitschr. angew. Chem.*, 1888, p. 376. [2] *Compt. rend.*, 1897.

[3] The titre of the iodine solution may be controlled by comparing the thiosulphate solution with iodine by the method used for determining the iodine number of fatty substances (*see* chapter on Fatty Materials) and then titrating the thiosulphate and iodine solutions.

[4] The reaction between zinc sulphide and iodine takes place thus: $Zn\,S + 2I = ZnI_2 + S$, so that 32 parts of sulphur require 257·7 parts of iodine or 1 gram of sulphur.

(3) 10 grams of pure sodium thiosulphate and 2 grams of ammonium carbonate are dissolved to 1 litre; 10 c.c. of the iodine solution are decolorised by about 15 c.c. of the thiosulphate solution.

(4) Starch paste.

*Titration of the thiosulphate solution.* The thiosulphate solution is run from a burette, with continual shaking, into a bottle like those shown at $EE^1$ (Fig. 13) containing 200 c.c. of zinc acetate solution and a measured volume (e.g., 10 c.c.) of the iodine solution. When a pale yellow colour is reached, the titration is completed in presence of starch paste. If 10 c.c. of the iodine solution require, say, 15 c.c. of the thiosulphate, 1 c.c. of the latter will be equivalent to $0{\cdot}01 \div 15 = 0{\cdot}00066$ gram of sulphur.

*Apparatus:* The apparatus shown in Fig. 13 is required, including:

Two Kipps, one for carbon dioxide and the other for hydrogen.

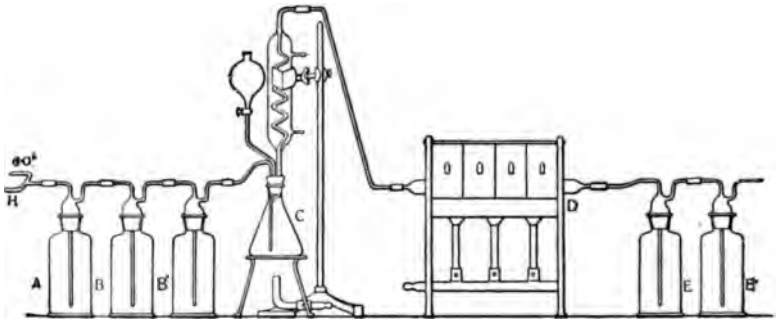


FIG. 13

A wash-bottle *A* containing about 150 c.c. of 2% silver nitrate solution; both gases are purified by passage through this solution.

Two wash-bottles *B* and $B^1$ containing about 100 c.c. of the 2% silver nitrate solution and distilled water respectively.

A flask *C* of 500 c.c. capacity (the Corleis flask used for determining the total carbon does well) furnished with a three-holed stopper, traversed by (1) a right-angled tube reaching almost to the bottom of the vessel and serving to conduct the hydrogen and carbon dioxide, (2) the stem of a tapped-funnel for introducing the acid to attack the metal, and (3) the end of a small condenser connected with a porcelain tube glazed internally which can be heated to cherry-redness in a suitable furnace *D*.

An absorption flask *E* containing 200 c.c. of the zinc acetate solution and a second $E^1$ containing 50 c.c. of the same solution and serving as check.

*Procedure.* The flasks *E* and $E^1$ being charged, 5 grams of the metal are placed in the flask and the air in the apparatus expelled by carbon dioxide. The porcelain tube is then gradually heated to redness and a mixture of 60 c.c. of dilute hydrochloric acid (1 vol. HCl to 2 vols. of water) with 30 c.c. of dilute sulphuric acid (1 vol. $H_2SO_4$ to 4 vols. of water) run in by means of the funnel. The acids are allowed to act for some time in the cold; in the meantime, the current of carbon dioxide is replaced by one

7·928 grams; 1 c.c. of the solution containing 7·928 grams of iodine per litre will, therefore, correspond with 0·001 gram of sulphur.

of hydrogen,[1] and after about 5 minutes the flask is gently heated to complete the action, which may occupy 15–30 minutes, according to the nature of the metal.

The hydrogen in the apparatus is then displaced by carbon dioxide. The bottle $E^1$ is then emptied and washed into $E$ and an exactly measured volume of the iodine solution (10, 20 or 30 c.c. according to the amount of the precipitate) added. After some time, during which the flask is occasionally shaken, the excess of iodine is titrated with the thiosulphate solution in the usual way.

Example : 10 c.c. of iodine solution were taken and 11 c.c. of thiosulphate solution were required to decolorise the excess of iodine. The sulphur has therefore absorbed iodine equivalent to $15 - 11 = 4$ c.c. of thiosulphate, the amount of sulphur thus being $0{\cdot}00066 \times 4$, and the percentage of sulphur in the sample $(4 \times 0{\cdot}00066 \times 100) \div 5 = 0{\cdot}053$.

This method gives excellent results and is simple to execute. It is especially advantageous when determinations have to be made regularly, since, when the apparatus is fitted up and the solutions ready, a determination can be made in about 30 minutes.

## 6. Determination of the Arsenic

Arsenic may be determined fairly simply by distilling as trichloride and titrating the distillate with iodine solution.

*Reagents :* (1) Solution of iodine in potassium iodide.[2]

2. Starch paste.

*Titration of the iodine solution.* According to Treadwell, the titre of the iodine solution with respect to arsenic is ascertained by dissolving, in the hot, 1·32 gram of arsenious acid (puriss.) in the least possible quantity of concentrated caustic soda solution, the liquid being transferred quantitatively to a litre flask, and a drop of phenolphthalein and sufficient dilute sulphuric acid to decolorise the liquid being added.

About 20 grams of sodium bicarbonate are dissolved in 500 c.c. of cold water and the solution filtered and added to that of the arsenious anhydride. If the liquid is still red, a few drops of dilute sulphuric acid are added and the volume made up to 1 litre : 1 c.c. of this solution contains 1 m. grm. of arsenic. Into 50 c.c. of this solution (0·050 gram arsenic) mixed with a little starch paste, the iodine solution is run from a burette until the liquid becomes blue ; the amount of arsenic corresponding with 1 c.c. of the iodine solution is then calculated.

*Procedure.* Into a distillation flask (about ½ litre) furnished with a lateral bulb-tube are introduced 5 grams of the sample, 3–5 grams of powdered potassium chlorate and then, gradually and with shaking and cooling, 80

[1] Some authors dispense with the current of hydrogen during the attack of the metal and merely drive the air from the apparatus before the action and displace the products of the reaction when the metal is completely dissolved, by means of a current of carbon dioxide.

[2] The iodine solution used for the volumetric determination of the sulphur (*see* p. 177) is suitable ; or 3·3858 grams of iodine and 10 grams of potassium iodide may be dissolved to 1 litre, 1 c.c. of this solution corresponding with 1 m. grm. of arsenic.

c.c. of hydrochloric acid (D = 1·19). When the action slackens, the flask is heated carefully on a water-bath until the smell of chlorine disappears and, when cold, 200 c.c. of hydrochloric acid (D 1·19) and 50 grams of ferrous chloride or, better, 25–30 grams of cuprous chloride, free from arsenic, are added.

To the neck of the distilling flask is fitted, by means of two grey rubber stoppers, an internal pressure regulator, consisting of an inverted flask rather less than half filled with concentrated hydrochloric acid and fitted with tubes $t$ and $t^1$ of about 6 mm. bore (*see* Fig. 14) which, if the pressure falls, allow air to enter the flask and rapidly to re-establish the equilibrium. The concentrated hydrochloric acid in the regulating flask, as it gradually becomes heated, further tends to increase the pressure and thus contributes to the regularity of the distillation.

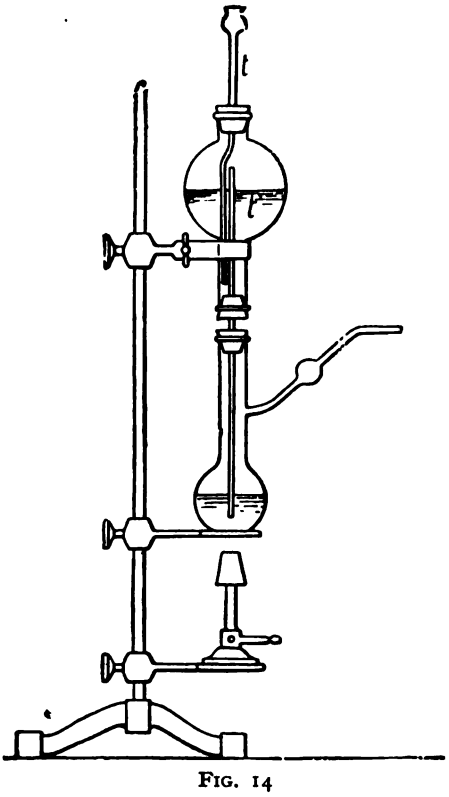

FIG. 14

The side-tube of the distilling flask—provided with a small bulb to prevent drops spurted from the boiling liquid from rising along the side-tube—is then connected with a 100 c.c. pipette, which dips for a few millimetres into boiled water rendered alkaline with 50–60 c.c. of ammonia (D 0·91) and mixed with a few drops of methyl orange, this being contained in a moderately large beaker standing in a bath of cold water. The flask is then heated and most of the liquid contained in it slowly distilled until the solution in the beaker, becoming acid, assumes a faintly red colour.

At this point the pipette is removed and rinsed out with a little water, the distillate being rendered alkaline by a slight excess of powdered sodium bicarbonate, mixed with a little starch paste and titrated with the iodine solution ; the proportion of arsenic in the metal is thus ascertained.

⁂

Cast-irons always contain marked quantities of impurities ; they are brittle and non-malleable.

*Grey cast-irons* are more or less dark in colour according to their content in graphitic carbon, and they have a granular structure, melt at about 1200° and have the specific gravity 7·0–7·2. They contain considerable proportions of silicon (from 1% in the paler products to 3–5% in the darker ones, the mean

being 1·5–2%). They are very rich in carbon (2–5%), which occurs entirely in the graphitic state in ordinary grey cast-irons, and partly combined in the lighter ones. They contain also small quantities of manganese (about 1%) and sometimes sulphur (0·01–0·1%) and phosphorus (0·05–1·8%). They serve in general for foundry purposes and those with little phosphorus for refining.

*White cast-irons* have a shining, white colour tending to grey, a crystalline, granular and, sometimes, radiating fibrous structure ; they melt at about 1100° and have the specific gravity 7·4–7·5. They contain 2–3·5% of carbon, largely combined, and only small quantities of silicon (0·5–1%), but they are very rich in manganese (1–5%), and sometimes contain considerable proportions of sulphur (0·1–0·25%) and phosphorus (more than 3%). They are usually employed for refining.

The products containing more than 5% of manganese are : *Spiegeleisen* (5–30% Mn, 0·2–1·2% Si and 4–5% C), *Silico-spiegel* (20% Mn, 10–12% or even more Si), and *Ferro-manganese* (30–85% Mn and up to 7·5% C).

*Malleable iron* represents the product of the refining of cast-iron, contains less than 2% of carbon and, according to its carbon content, to its uses, and to its hardness, elasticity, strength, etc., is subdivided into : *soft iron* (*soft wrought-iron* or *mild steel*, according to the mode of preparation), which is very ductile and malleable and contains less than 0·3–0·5% of carbon ; and *steel* (cementation or blister steel, crucible steel, cast steel, etc.), which has larger amounts of carbon (more than 0·3–0·5%) and is ductile and malleable, but very hard, elastic and resistant and capable of being hardened. Steels with more than 1·5% of carbon begin to lose their malleability and become brittle.

Small quantities of *silicon* increase the hardness of malleable iron but diminish its malleability (a good malleable iron should not contain more than 0·1–0·2%). Most harmful for malleable iron are *phosphorus*, which even in small quantities (0·1%) renders it cold short, and *sulphur*, which renders it red short even in the proportion of 0·05–0·1%. *Manganese* diminishes the harmful effects of sulphur and hence improves the quality of iron and steels. Injurious actions are also exerted by arsenic, tin, antimony, copper (beyond 0·4%), oxygen, etc.

The following table gives the compositions of various commercial types of soft iron and steel.

TABLE VIII

**Compositions of Various Iron and Steels (percentages)**

| | C | Si | Mn | P | S |
|---|---|---|---|---|---|
| Swedish iron . . . | 0·02–0·07 | <0·01–0·02 | 0–0·15 | Trace–0·02 | 0·01–0·02 |
| Wrought-iron . . . | 0·16 | 0·02 | 0·09 | 0·09 | Trace |
| Wrought steel . . . | 0·90 | 0·10 | 0·25 | 0·07 | Trace |
| Ingot iron for construction . . . . . | 0·08–0·25 | <0·02 | 0·4–0·6 | <0·08 | <0·08 |
| Ingot steel for rails . | 0·30–0·50 | 0·05–0·20 | 0·5–1·0 | <0·08 | <0·08 |
| Martin steel for castings | 0·30–0·60 | 0·20–0·60 | 0·5–1·0 | 0·1 | — |
| Crucible tool steel . . | 0·7–1·2 | 0·1–0·2 | 0·1–0·3 | <0·04 | <0·03 |

## SPECIAL STEELS

*Special* or *high-speed* steels, now largely used, are characterised by the presence of some suitable element, such as chromium, tungsten, nickel, etc., which confers quite special properties. The chemical analysis of special steels includes, therefore, besides the ordinary determinations, those of the specific elements present. Tests will first be given for the identification of these elements.

### Qualitative Tests

**1. Detection of Chromium.**—A little of the finely powdered sample is heated on the cover of a platinum crucible or in a porcelain dish and the residue fused with sodium carbonate and nitre. In presence of chromium a more or less intensely yellow mass is obtained. If a solution (which should be acid) of this in dilute acetic acid is treated with silver nitrate, a brick-red precipitate is obtained.

**2. Detection of Nickel.**—A little of the sample is dissolved in hydrochloric acid, the iron oxidised with nitric acid and a little tartaric acid (2 grams per 0·5 gram of the steel) dissolved in a little water added. The liquid is then made alkaline with ammonia and heated with a little 1% solution of dimethylglyoxime in alcohol: a red precipitate indicates nickel.

**3. Detection of Manganese.**—(*a*) A little of the finely powdered sample is heated on a platinum crucible cover or in a porcelain dish and the residue fused with sodium carbonate and nitre. (*b*) The sample is treated with nitric acid (D 1·2) and the solution heated with a little lead peroxide free from manganese. When the peroxide settles, the liquid will exhibit a violet-red colour if manganese is present. This reaction is very sensitive and with ferro-manganese, a very small quantity must be taken.

**4. Detection of Tungsten.**—A little of the finely powdered sample is fused with sodium carbonate and nitre, the mass being taken up in hot water and the solution filtered, acidified strongly with hydrochloric acid and heated. In presence of tungsten, a white precipitate is obtained, turning yellow on heating; this consists of anhydrous tungstic acid and is soluble in sodium carbonate.

**5. Detection of Vanadium.**—A little of the sample is dissolved in nitric acid (D = 1·18) and a small quantity of hydrogen peroxide allowed to flow down the side of the tube. In presence of vanadium, a reddish-brown coloration is formed at the zone of contact of the two liquids.

**6. Detection of Molybdenum.**—A little of the finely powdered sample is heated and the residue fused with sodium carbonate and nitre, the mass being treated with hot water and filtered. The filtrate is strongly acidified with sulphuric acid, evaporated and heated until white fumes appear. A little conc. sulphuric acid is stirred into the cold liquid and, without diluting, alcohol is added. In presence of molybdenum an intense blue coloration is obtained. This coloration disappears on dilution with water, and if the liquid is then subjected in the hot to the action of hydrogen sulphide, a brown precipitate of molybdenum sulphide is obtained.

**7. Detection of Silicon.**—The sample is ground with sodium carbonate and nitre and the mass dissolved in dilute hydrochloric acid and evaporated to dryness. After being heated for an hour in an oven at 120–130°, the residue is treated with hot dilute hydrochloric acid and filtered. In presence of silicon, a more or less abundant residue of silica, attackable by hydrofluoric acid, remains. Ferro-silicon with a high proportion of silicon is dissolved in 10% sodium hydroxide solution.

**8. Detection of Titanium.**—A little of the sample is dissolved in nitric acid and evaporated to dryness, the residue being ignited to decompose nitrates. The oxides thus obtained are fused with bisulphate, the cooled mass being dissolved in cold water, acidified with sulphuric acid and treated with hydrogen peroxide. In presence of titanium a distinctly yellow coloration is exhibited.

**9. Detection of Aluminium.**—A little of the sample is dissolved in hydrochloric acid diluted with an equal volume of water, a few drops of nitric acid being added (to oxidise the iron), the liquid rendered alkaline with sodium hydroxide, diluted, boiled for some time and filtered. When the filtrate is heated with excess of ammonium chloride, a gelatinous precipitate of aluminium hydroxide is obtained if aluminium is present.

## CHROME STEELS

Chrome steels are hard and highly resistant to ordinary acids, and are used particularly for the manufacture of tools, projectiles, cylinders, etc. Their analysis includes, besides the ordinary determinations, that of chromium.

**1. Determination of the Chromium.**—The commonest methods for estimating chromium in steels consist in transforming the chromium into chromic acid or alkaline chromate and in determining the latter volumetrically. Owing to its accuracy and rapidity, the iodometric method is to be recommended. In presence of vanadium and molybdenum, which often accompany chromium in steels, the method is slightly modified to get rid of these metals, which behave towards iodine as chromium does.

*Reagents*: (1) N/10-potassium dichromate solution, prepared by dissolving 4·9033 grams of the salt—recrystallised in small crystals and dried at 130°—in water to 1 litre.

(2) Approximately N/10-sodium thiosulphate, 25 grams being dissolved to 1 litre.

(3) Starch paste.

*Titration of the thiosulphate.* To establish the titre of the thiosulphate solution with respect to the dichromate, and hence with respect to chromium, 20 c.c. of the dichromate solution (corresponding with 0·09806 gram of dichromate) are measured out, and 10 c.c. of 10% potassium iodide (free from iodate) [1] solution and 5 c.c. of hydrochloric acid (D 1·1) added, the liquid being then shaken and, after addition of 200–250 c.c. of water, titrated with the thiosulphate solution; starch paste is added towards the end of

[1] An aqueous solution of the potassium iodide, acidified with hydrochloric acid and mixed with a little starch paste, should remain colourless.

the titration. The volume of thiosulphate used corresponds with 0·09806 gram of potassium dichromate, and hence with 0·03466 gram of chromium.

(*a*) DETERMINATION OF THE CHROMIUM IN ABSENCE OF VANADIUM AND MOLYBDENUM. 2 grams of the sample, in a small porcelain dish covered with a clock-glass, are dissolved in nitric acid of D = 1·18 and the solution evaporated to dryness and the residue ignited to decompose the nitrates. When cold, the oxides are transferred quantitatively with a platinum spatula to an agate mortar in which they are mixed with sodium peroxide, the dish being repeatedly cleaned in the dry with small quantities of the peroxide (of which not more than 10–15 grams should be used altogether). The last traces of oxides adherent to the dish are removed by heating with a little dilute sodium hydroxide solution, the alkaline solution together with the water used to wash out the dish being transferred to a beaker.

The peroxide mixture is heated gently to fusion in a covered nickel or porcelain crucible, the heating being then continued for about 15 minutes at dull red heat. The cold crucible is treated in a covered beaker with hot water in which the mass rapidly dissolves, the alkaline liquid used for the final washing of the dish being then added, the crucible withdrawn and washed and the beaker kept for 1–2 hours on a steam-bath. If the solution appears greenish, owing to the presence of manganates, the latter are reduced by addition of a little sodium peroxide. The liquid is then made up to about 200 c.c., allowed to cool and filtered by decantation, the filtrate being collected in a 500 c.c. flask and the residue washed repeatedly with dilute sodium carbonate solution.[1] When the washing is completed, the filtrate is boiled to decompose any traces of sodium peroxide still present and, after cooling, made up to volume.

To 100 c.c. of this solution (0·4 gram of the sample), acidified with hydrochloric acid, are added 10 c.c. of 10% potassium iodide solution, the liquid being then diluted to 200–300 c.c. and the free iodine titrated with thiosulphate as before.

(*b*) DETERMINATION OF THE CHROMIUM IN PRESENCE OF VANADIUM AND MOLYBDENUM. When the oxidation of the chromium by fusion with sodium peroxide (*see a*, above) is complete, the aqueous extract—which may contain alkaline vanadates and molybdates in addition to chromate—is neutralised exactly with nitric acid (towards methyl orange), heated to boiling and treated with a slight excess of 10% mercurous nitrate solution. Under these conditions the chromium, vanadium, molybdenum, tungsten and phosphorus are precipitated.

The liquid is heated to boiling and, when the precipitate has settled, mercurous nitrate solution is added to ascertain if the precipitation is complete. In case the solution has become acid, it is neutralised with a few drops of ammonia and filtered, the precipitate being washed first with water and then with very dilute mercurous nitrate solution. The filter and the whole of the precipitate, in an open platinum crucible, are then

[1] If traces of chromium still remain in the residue, the latter is fused with sodium and potassium carbonates, the resulting product extracted and the new solution added to that of the first treatment.

incinerated in an efficient draught-chamber to expel the mercury. The residue is strongly ignited, allowed to cool, mixed in the crucible with 8–10 parts of a mixture of 4 parts of sodium carbonate with 1 part of potassium bitartrate, and heated carefully so as not to burn the carbonaceous residue entirely away.

The chromium then remains as oxide, whilst the vanadium, molybdenum and tungsten form the sodium salts of the respective acids. The crucible is next heated with water in a beaker, the crucible extracted and the insoluble residue of chromic oxide and carbon filtered off, washed first with water containing a little sodium carbonate and then with water acidified with nitric acid, dried and ignited in a tared platinum crucible. The chromic oxide thus obtained may be weighed directly. The result may be controlled volumetrically by heating the oxide with a mixture of sodium carbonate and magnesium oxide (*see* Ferro-silicon), dissolving the resultant mass in hydrochloric acid, making up to volume in a 500 c.c. measuring flask and titrating the chromium in an aliquot part (*see* 1, *a*).

**2. Determination of the Carbon, Silicon, Phosphorus, Sulphur and Arsenic.**—The methods used for ordinary steels are applicable (*see* Iron, 1, 2, 4, 5 and 6).

**3. Determination of the Manganese.**—The residue remaining undissolved on lixiviation of the fused mass (*see* 1, *a*) is dissolved in hydrochloric acid and the manganese determined in this solution, which contains also all the iron (*see* Ferro-silicon, 3).

***

Chrome steels may contain 0·3–4% of chromium (usually 1–2%), 0·3–1·6% of carbon, 0·05–0·3% of silicon, 0·5–1% of manganese, and traces of phosphorus and sulphur (0·01–0·04%). Extra hard steels contain 2–3% of chromium and 1·5–1·6% of carbon. Nickel, vanadium, tungsten, silicon, etc., are often associated with the chromium (chrome-nickel, chrome-vanadium, chrome-tungsten, chrome-silicon, etc., steels).

It should be noted that small proportions of chromium (less than 0·1%) are found in almost all ordinary steels.

The following table gives the percentage compositions of some commercial samples of chrome steels (Geiger) :

TABLE IX

**Composition of Chrome Steels**

| No. | C | Si | Mn | P | S | Cr |
|---|---|---|---|---|---|---|
| 1 . . . | 0·311 | 0·149 | 0·98 | 0·039 | 0·031 | 0·361 |
| 2 . . . | 0·382 | 0·279 | 1·03 | 0·035 | 0·042 | 1·045 |
| 3 . . . | 0·895 | 0·280 | 0·97 | 0·018 | 0·014 | 0·480 |

## NICKEL STEELS

Nickel steels are valued particularly on account of their strength and elasticity.

Their analysis includes determinations of the usual elements of ordinary steels and also of the nickel and, sometimes, chromium and tungsten.

**1. Determination of the Nickel by means of Dimethylglyoxime.**—In a solution which is either ammoniacal or faintly acid with acetic acid, dimethylglyoxime precipitates nickel quantitatively as nickeloxime; this is a red, crystalline precipitate which can readily be collected on a Gooch crucible, washed and weighed.

*Procedure.* With steels containing less than 3% Ni, 2 grams, or proportionately less with richer steels,[1] are treated in a porcelain dish, covered with a clock-glass, with nitric acid (D 1·2). The solution is evaporated to dryness and the residue calcined and taken up in hydrochloric acid as indicated for the determination of silicon in steels and cast-iron (*see* p. 172).

To the hydrochloric acid solution, freed from silica and diluted to 250–300 c.c., are added about 7 grams of tartaric acid dissolved in a little water for each gram of metal taken, the liquid being then rendered alkaline with dilute ammonia so as to give a perfectly clear solution.

The latter is then again slightly acidified with hydrochloric acid, heated almost to boiling and 10–20 c.c. of a 1% solution of dimethylglyoxime in alcohol (0·05 gram of nickel requires about 20 c.c.) added drop by drop and with shaking; ammonia is then added until the liquid just smells distinctly. The nickel is separated as a voluminous, crystalline precipitate. After a few minutes, 5–10 c.c. of the dimethylglyoxime are added to ascertain if the precipitation is complete, and when this is so the liquid is heated for about 30 minutes on a water-bath and, when cold, filtered through a Gooch crucible. The precipitate is washed repeatedly with hot water, dried at 120° and weighed; the weight obtained, multiplied by 0·2032 gives the amount of nickel in the sample taken.[2]

**2. Determination of the Carbon, Phosphorus, and Sulphur.**—*See* Iron, 1, 4, 5.

**3. Determination of the Silicon.**—The silica separating when the metal is treated with nitric acid, is weighed (*see* above and Iron, 2).

**4. Determination of the Manganese.**—In presence of small quantities of nickel, the manganese may be determined by Volhard's volumetric method (*see* p. 197).

If, however, nickel is present in large quantities, the sample is dissolved in hydrochloric acid and the iron eliminated by treatment with ether in Rothe's apparatus, the nickel being then separated from the manganese by means of ammonia and bromine water.

[1] For steels with 10–25% of nickel, it is advisable to use 1 gram and, after elimination and, if required, estimation of the silica, to make up to a definite volume and take an aliquot part containing about 0·05 gram of nickel for the determination.

[2] For the volumetric determination of nickel in steels, *see* Belasio and Marchionneschi, *Annali di Chim. Applicata* 1914, I, p. 133.

**5. Determination of the Chromium.**—*See* Analysis of Chrome-nickel Steels.

**6. Determination of the Tungsten.**—The tungsten is first separated as tungstic acid on the lines indicated for the analysis of tungsten steels (*see* p. 188) and the nickel in the filtrate estimated by the method given above.

***

Nickel steels usually contain 0·5–10% Ni but the content may reach 25%, especially in steels for armour-plating, or even more (*invar* contains 46% Ni and 0·15% C). Chromium is often associated with the nickel (chrome-nickel steels).

The following results are given by Geiger:

TABLE X

**Composition of Nickel Steels (percentages)**

| Nickel Steel for | C | Si | Mn | P | Si | Ni |
|---|---|---|---|---|---|---|
| Ball mills . . . . . | 0·07 | 0·345 | 0·65 | 0·045 | 0·057 | 0·246 |
| Brakes. . . . . | 0·361 | 0·280 | 0·68 | 0·023 | 0·035 | 3·85 |
| Gun barrels (American) . . | 0·39 | 0·197 | 0·75 | 0·02 | 0·032 | 2·62 |
| Toothed wheels . . . . | 0·25 | 0·216 | 0·52 | 0·011 | 0·019 | 1·85 |

## MANGANESE STEELS

Manganese steels are valued for their hardness and strength, and have properties analogous to those of nickel steels and are less costly. From the analytical standpoint they may be regarded as ordinary steels very rich in manganese.

**1. Determination of Silicon and Manganese.**—2·5 grams of the sample are treated with nitric acid (D 1·18) and the liquid evaporated to dryness, calcined, and taken up in hydrochloric acid, the solution being again evaporated and the residue heated at 135° to render the silica completely insoluble. The subsequent procedure is as indicated on p. 172.

The filtrate is collected in a measuring flask and the manganese present determined either by Volhard's volumetric method or electrolytically (*see* later, Ferro-manganese).

**2. Determination of the Carbon, Phosphorus and Sulphur.**—*See* Iron, 1, 4, 5.

***

The percentage compositions of certain manganese steels in common use are (Geiger):

TABLE XI

**Composition of Manganese Steels**

| No. | C | Si | Mn | P | S |
|---|---|---|---|---|---|
| 1 . . | 0·320 | 0·311 | 6·32 | 0·077 | 0·036 |
| 2 . . | 0·585 | 0·265 | 9·61 | 0·086 | 0·042 |
| 3 . . | 0·804 | 0·280 | 8·70 | 0·034 | 0·015 |
| 4 . . | 1·085 | 0·241 | 12·24 | 0·068 | 0·012 |

## TUNGSTEN STEELS

Tungsten steels are very hard and serve specially for making tools, permanent magnets, etc. Their analysis includes estimations of the ordinary elements of steel and also of tungsten.

**1. Determination of the Silicon and Tungsten.**—When tungsten steel is treated with nitric acid, the silicon present separates as silica and the tungsten as tungstic acid. After weighing, the precipitate is treated with hydrofluoric acid, the loss representing the silica and the remainder the tungstic acid.

*Procedure.* 2–5 grams of the finely powdered sample are treated in a covered dish with nitric acid (D 1·18), the solution being evaporated and the residue ignited to decompose the nitrates and taken up in hydrochloric acid. The liquid is then evaporated to dryness, the silica rendered insoluble at 135°, as under 2, p. 172. The residue is moistened with conc. hydrochloric acid and then just sufficient hydrochloric acid (D 1·12) added to dissolve the ferric oxide in the hot. The liquid is evaporated to a syrup, allowed to cool, diluted with about double its volume of water acidified with hydrochloric acid and, after a few minutes, filtered by decantation. The precipitate is afterwards introduced on to the filter and washed with water acidified with hydrochloric acid until the liquid passing through no longer gives the reaction for iron with thiocyanate.[1] After being dried, the filter and precipitate are incinerated in a platinum crucible and the residue ignited at not too high a temperature (not in the blowpipe flame) and weighed.

To eliminate and estimate the silica, the weighed mixture of tungstic acid and silica is treated with a little sulphuric acid and a few c.c. of hydrofluoric acid and the procedure indicated on p. 171 then followed.

The loss of weight gives the silica and this, multiplied by 0·4693 the silicon ; the residue is the tungstic acid, multiplication by 0·7931 giving the tungsten.

If the sample contains more than 10–15% of tungsten, it is difficult to attack with nitric acid and it is then advisable to have recourse to fusion (*see* later: Ferro-tungsten).

[1] A yellow ring of tungstic acid, difficult to remove merely by washing, is often formed in the dish. This may be detached by gentle rubbing with a piece of filter paper moistened with ammonia, the paper being then added to the rest of the precipitate.

Further, there are some types of tungsten steel, especially the chrome-tungsten steels, which, although they have not a high content of tungsten, are difficult to dissolve in nitric acid. In such cases, when the action of the nitric acid ceases, a few drops of conc. hydrochloric acid are added, this being repeated until the attack of the metal is complete.

The tungstic acid freed from silica may often contain small amounts of iron and chromium. In this event, the weighed residue is fused with sodium-potassium carbonate, the mass treated with hot water and the insoluble residue, consisting of ferric oxide, filtered off, washed, ignited and weighed. The chromium is determined volumetrically in the filtrate (*see* p. 183).

**2. Determination of the Carbon.**—For products readily attacked by acids, the Corleis method may be used, whilst, for the others, direct combustion in a current of oxygen must be employed (*see* Iron, 1).

**3. Determination of the Manganese, Phosphorus and Sulphur.**—The determination of these elements may be effected by the methods described under Iron, 3, 4 and 5. For some determinations, such as that of the phosphorus, use may be made of the hydrochloric acid solution from which the silica and tungstic acid have been removed.

***

Tungsten steels usually contain 2–10% of tungsten (but sometimes 20% or more), 0·5–1·5% of carbon, 0·2–0·7% of silicon, 0·4–2·5% of manganese and, in some cases, small quantities of phosphorus ; a good tungsten steel should not, however, contain more than 0·015% of phosphorus.

Cast-and wrought-iron, and ordinary steels do not usually contain tungsten.

## VANADIUM STEELS

Owing to their hardness and their resistance to shock and vibration, vanadium steels are used for the framework of locomotives, automobile parts, tools, etc.

Their analysis includes estimations of the elements normally present in steels (carbon, silicon, manganese, phosphorus, sulphur, etc.) as well as that of vanadium and, sometimes, of nickel, chromium and molybdenum, which very often accompany vanadium in special steels.

**1. Determination of the Vanadium.**—If the vanadium is transformed, by fusion with an oxidising agent, into vanadic acid, it may be determined, according to Holverscheit, iodometrically ; the vanadic acid is reduced by means of hydrobromic acid, the bromine liberated in the reaction [1] being collected in potassium iodide solution and the iodine thus set free titrated with thiosulphate.

*Procedure.* 2–3 grams of the sample are dissolved in nitric acid (D 1·18) in a small porcelain dish, the liquid evaporated to dryness, the residue ignited and the oxides obtained fused in a nickel crucible with 12–18 grams of sodium peroxide, as described for chrome steels. The mass obtained is lixiviated with hot water and the residue insoluble in water dried and

[1] $V_2O_5 + 2HBr = V_2O_4 + H_2O + Br_2$.

fused with sodium carbonate in a platinum crucible, this mass being also lixiviated with water.

The two aqueous solutions, which contain all the vanadium as sodium vanadate, are together boiled to decompose the excess of peroxide, evaporated to 30–40 c.c., and poured into the flask of the Bunsen apparatus (*see* Fig. 15), the vessel being rinsed out with very little water.

The alkaline liquid is neutralised with conc. hydrochloric acid free from chlorine, the yellowish solution being then mixed with 30 c.c. of conc. hydrochloric acid and 1–3 grams of potassium bromide. The apparatus is arranged as shown in the figure, the conducting tube from the flask being dipped into the potassium iodide solution (5–10 grams of potassium iodide free from iodate) contained in the retort fixed so as to be rotatable.

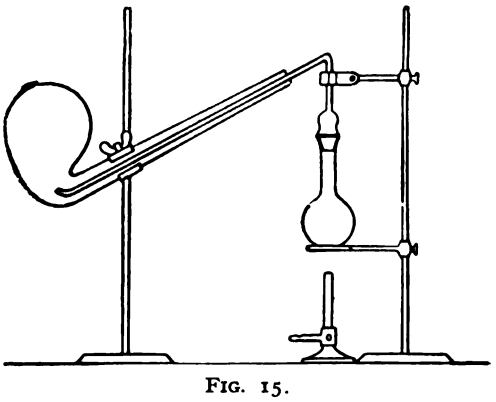

FIG. 15.

The liquid is then slowly heated to boiling, the retort being turned at intervals to expel the accumulated air; the boiling is continued for about 10 minutes. Without interrupting the heating, the retort is removed, the conducting tube being rinsed with water. The retort is then cooled, emptied into a beaker and rinsed out several times, first with water and then with potassium iodide solution. The liberated iodine is titrated with thiosulphate in the usual way: 1 c.c. N/10-thiosulphate = 0·005106 gram of vanadium.[1]

If the liquid from the lixiviation of the fused mass appears yellow owing to the presence of chromates, it is necessary to eliminate the chromium before titrating the vanadium. After the liquid has been boiled to decompose the excess of sodium peroxide, it is neutralised exactly with nitric acid and treated with mercurous nitrate to precipitate the chromium, vanadium, etc. (*see* Analysis of Chrome Steels). The precipitate is collected on a filter and washed and ignited in a platinum crucible to expel the mercury, the residue being fused with sodium carbonate and bitartrate and the resultant mass lixiviated with hot water. In the residue insoluble in water the chromium is determined, and in the alkaline solution the vanadium, by the method already given.

**2. Determination of the Carbon, Silicon, Manganese, Phosphorus and Sulphur.**—*See* Analysis of Ordinary Steels (Iron, 1, 2, 3, 4, 5).

**3. Determination of the Nickel.**—As in nickel steels.

**4. Determination of the Molybdenum.**—When the reduction of

[1] If the vanadium is present in very small quantity, it is necessary to dissolve 10–15 grams of the sample in hydrochloric acid, to eliminate the iron by means of ether in Rothe's apparatus, to evaporate the hydrochloric acid solution containing the vanadium with sulphuric acid and to fuse the sulphates obtained with sodium hydroxide and sodium peroxide to transform the vanadium into sodium vanadate.

the vanadic acid is complete, the liquid in the flask—which contains the vanadium as vanadyl salt and the molybdenum as molybdic acid—is treated with hydrogen sulphide in a pressure bottle; the molybdenum sulphide precipitated is collected in a Gooch crucible, transformed into the trioxide as in the determination of molybdenum in molybdenum steels, and weighed.

**5. Determination of the Chromium.**—*See* above, p. 190.

***

The vanadium content of vanadium steels is usually about 0·2% and scarcely ever exceeds 1%.

Chromium and nickel are often associated with the vanadium, chrome-vanadium, nickel-vanadium and chrome-nickel-vanadium steels possessing the valuable properties of vanadium steels along with those of chrome and nickel steels.

Small quantities of vanadium may be found in ordinary cast-irons when vanadiferous ores have been used for their manufacture.

The compositions of certain vanadium, nickel-vanadium, and chrome-nickel-vanadium steels are as follows (Mars, Geiger):

TABLE XII

**Composition of Vanadium Steels**

| | C | Si | Mn | P | S | Ni | Cr | Va |
|---|---|---|---|---|---|---|---|---|
| *Vanadium steels* | | | | | | | | |
| For locomotive frame-works . . . . . | 0·28 | 0·28 | 0·57 | — | — | — | — | 0·22 |
| For tools and instruments . . . . . | 1·20 | 0·20 | 0·25 | — | — | — | — | 0·6–1·0 |
| *Nickel-vanadium steels* | | | | | | | | |
| For toothed gearing for automobiles . . . | 0·052 | 0·316 | 0·67 | 0·012 | 0·028 | 6·68 | — | 0·26 |
| *Chrome-nickel-vanadium steels* | | | | | | | | |
| For automobile hubs . | 0·068 | 0·184 | 0·48 | 0·026 | 0·033 | 5·72 | 1·18 | 0·19 |

## MOLYBDENUM STEELS

Molybdenum steels are highly ductile, elastic and resistant to breaking, and are therefore mostly used for tools, although the cheaper tungsten steels are usually preferred for this purpose.

Their analysis includes, besides determinations of the elements usual in ordinary steels (carbon, silicon, manganese, phosphorus, sulphur), also that of molybdenum and, sometimes, of tungsten, chromium, nickel, etc.

**1. Determination of the Molybdenum.**—When the iron has been separated from the molybdenum by fusion with sodium peroxide and lixiviation of the product with water, the molybdenum is precipitated in the

aqueous solution by hydrogen sulphide, the sulphide separated and ignited to the trioxide, which can be purified if necessary and weighed.

*Procedure.* 2–3 grams of the sample are treated, in a small, covered porcelain dish, with nitric acid (D = 1·18), the solution evaporated to dryness, the residue ignited gently to decompose the nitrates, and the oxides obtained fused with sodium peroxide in a nickel crucible, as indicated for the analysis of chrome steels. The mass is lixiviated with hot water, sodium peroxide being added if the mass appears greenish owing to the presence of manganates, and the liquid boiled and filtered, hot water being used for washing.

The residue is dried and fused with sodium carbonate, and the fused mass lixiviated with hot water to recover any small quantities of molybdenum remaining in the residue insoluble in water. The two liquids—which may contain, besides the molybdenum as sodium molybdate, also vanadium, tungsten, chromium, phosphorus, silicon, etc.—are united and, if in presence of large quantities of molybdenum, made up to a definite volume, of which an aliquot part is taken for the determination ; where, however, the quantity of molybdenum is small, the whole of the filtrate is taken.

The volume of the solution is reduced to 50–60 c.c., most of the alkali neutralised with sulphuric acid, 25 c.c. of concentrated ammonia solution added and the solution treated with hydrogen sulphide. After some time the liquid is acidified with dilute sulphuric acid,[1] heated to boiling and allowed to cool, the current of hydrogen sulphide being continued throughout. The molybdenum sulphide is filtered through a tared Gooch crucible, washed first with water acidified with sulphuric acid and then with alcohol, and dried at 100°. The crucible, covered with a clock-glass, is placed in a fairly roomy nickel crucible and heated with a small flame to convert the molybdenum sulphide into trioxide. As soon as the odour of sulphur dioxide ceases, the clock-glass is removed and the heating continued to constant weight, the base of the nickel crucible being kept incandescent.

The weight of the molybdenum trioxide—which is pale yellow if pure —multiplied by 0·6667, gives the molybdenum present.

In some cases the molybdenum trioxide may contain small quantities of silica. In such case the weighed trioxide is dissolved in ammonia in the crucible, the residual silica being washed, dried and weighed. If vanadium is present (brown coloration of the trioxide) the weighed oxides are dissolved in a little sodium hydroxide solution and the vanadium determined in the alkaline solution (*see* Vanadium Steels), the weight of the vanadium pentoxide ($V_2O_5$) being subtracted from that of the molybdenum trioxide found.

**2. Determination of the Silicon and Tungsten.**—The procedure followed is that given for estimating these elements in tungsten steels.

**3. Determination of the Carbon, Manganese, Phosphorus and Sulphur.**—The methods used with ordinary steels are applicable (*see* Iron, 1, 3, 4, 5).

**4. Determination of the Chromium.**—The chromium is estimated in an aliquot part of the aqueous solution from the lixiviation of the mass

[1] If tungsten is present, acidification is preceded by addition of a little tartaric acid to prevent the precipitation which would otherwise occur.

after fusion with sodium peroxide, the method employed being that given on p. 184 for the determination of chromium in presence of molybdenum.

**5. Determination of the Nickel.**—The method used in the case of nickel steels is employed.

***

Molybdenum steels contain on the average 0·5–5% of molybdenum (rarely 10–12%), with which chromium, nickel, etc., are often associated, and they contain the proportions of carbon, silicon, phosphorus, etc., normally present in ordinary steels.

Molybdenum steels with 3–4% Mo and 1–1·5% C serve also for making permanent magnets.

## SILICON STEELS

Silicon steels have a very high elastic limit and great resistance to shock and are therefore used for making springs.

Their analysis includes essentially determinations of the silicon and carbon and of the other elements usually present in steels (Mn, P, S, etc.).

Each of these determinations may be carried out just as with wrought-iron, steel and cast-iron (*see* Iron).

***

The two commonest types of silicon steel contain respectively: (1) 0·45–0·5% C and 1·5–1·2% Si and (2) 0·65–0·7% C and 0·9–0·8% Si. Silicon steels with 2–3% Si and free from graphitic carbon, are used for dynamo sheet, rails, etc.

## CHROME-NICKEL STEELS

Chrome-nickel steels exhibit the hardness of chrome steels and the strength of nickel steels. They are used, therefore, for making machine parts exposed to great stress, armour-plating, projectiles, etc.

**1. Determination of the Chromium and Nickel.**—These are estimated on two separate portions of the sample by the methods given for chrome steel and nickel steel.

**2. Determination of the Carbon, Silicon, Manganese, Phosphorus and Sulphur.**—As with chrome steels and nickel steels.

***

Chrome-nickel steels for machine parts have the following mean composition: 0·2–0·5% Cr, 2·5–2·8% Ni, 0·35% C; those for armour-plating: 0·2–0·9% Cr, 1·7–2·8% Ni, 0·2–0·4% C; and those for projectiles, 0·65–2% Cr, 2–2·6% Ni and 0·6–0·8% C.

## CHROME-TUNGSTEN STEELS

These have the property of retaining their temper even at high temperatures and are, therefore, used especially for making tools for metal working.

**1. Determination of the Chromium and Tungsten.**—2–3 grams of the sample are treated with nitric acid, evaporated and calcined, the oxides obtained being fused with sodium peroxide as for chrome steels.

The product of the fusion is lixiviated with water and the solution made up to volume in a measuring flask. In an aliquot part the chromium is determined as indicated for the estimation of chromium in chrome steels (the tungstic acid present does not interfere with the titration). In another aliquot part the chromium and tungsten are precipitated with mercurous nitrate (*see* Chrome Steels), the precipitate being calcined to eliminate the mercury and the residue of tungsten trioxide and chromic oxide weighed; the tungsten is thus obtained by difference. It is well to ascertain by treatment with hydrofluoric and sulphuric acids that no silica is present with the chromium and tungsten oxides.

**2. Determination of the Carbon, Silicon, Manganese, Phosphorus and Sulphur.**—As with chrome or tungsten steels.

***

The percentage compositions of some of the chrome-tungsten steels which are most used are:

TABLE XIII

**Composition of Chrome-tungsten Steels**

| No. | W | Cr | Fe | C | Si | Mn |
|---|---|---|---|---|---|---|
| 1 | 15·5 | 4·5 | 79·0 | 0·43 | 0·22 | 0·17 |
| 2 | 13·5 | 8·0 | 77·0 | 0·60 | 0·40 | 0·30 |
| 3 | 12·0 | 3·0 | 83·0 | 0·71 | 0·20 | 0·30 |
| 4 | 9·5 | 2·05 | 88·0 | 0·45 | 0·60 | 0·18 |
| 5 | 7·0 | 2·1 | 90·0 | 0·20 | 0·25 | 0·18 |

## CHROME-VANADIUM STEELS

These exhibit all the valuable properties of both vanadium and chrome steels and are used for machine parts subjected to sudden stress and shock, such as automobile parts, springs, etc.

**1. Determination of the Chromium and Vanadium.**—As in vanadium steels containing chromium.

**2. Determination of the Carbon, Silicon, Manganese, Phosphorus and Sulphur.**—As with chrome or vanadium steels.

***

The percentage compositions of certain types of chrome-vanadium steels are as follows (Geiger, Eschard):

TABLE XIV

**Composition of Chrome-vanadium Steels**

| Used for | C | Si | Mn | P | S | Cr | V |
|---|---|---|---|---|---|---|---|
| Automobile framework . . | 0·263 | 0·116 | 0·43 | 0·013 | 0·009 | 0·934 | 0·18 |
| Drills . . . . . | 0·518 | 0·208 | 0·86 | 0·027 | 0·016 | 1·265 | 0·16 |
| Springs . . . . . | 0·44 | 0·173 | 0·83 | — | — | 1·044 | 0·18 |

## FERRO-METALLIC ALLOYS

*Ferro-metallic alloys* are forms of cast-iron, obtained in the blast furnace or the electric furnace and containing, besides iron, larger or smaller proportions of some special element. They are used for the preparation of special steels (e.g., ferro-chromium, ferro-tungsten, etc.) or for the refining of cast-iron or steel (e.g., ferro-silicon, ferro-aluminium, etc.). The qualitative investigation of the elements present is made as with special steels (*see* p. 182).

## FERRO-SILICON

This is generally prepared by fusion in the electric furnace of a mixture of sand, coke and ferric oxide, and serves for the refining of cast-iron and steel. The aim of the analysis is usually to establish the percentage of silicon, but sometimes determinations are required of the impurities present, e.g., carbon, manganese, phosphorus, sulphur, etc.

The types of ferro-silicon on the market nowadays are mostly of high silicon content (more than 25–30%) and are therefore insoluble or incompletely soluble in acids, so that they must be fused with alkali.

**1. Determination of the Silicon.**—Two methods are available:

(*a*) FUSION WITH SODIUM CARBONATE AND PEROXIDE.[1] An intimate mixture of 0·3–0·5 gram of the sample with 12–15 parts of sodium peroxide (free from silica) and 6–7 parts of anhydrous sodium carbonate is heated in a fairly large, covered nickel crucible, at first very carefully. When the reaction begins to slacken, the temperature is gradually raised, the crucible being heated round the walls rather than at the bottom, so that the mass fuses quietly.

The cold crucible is treated in a dish with hot water, the crucible being removed and washed and the solution, rendered distinctly acid with hydrochloric acid, evaporated to dryness in a porcelain dish. The residue is heated in an oven at 135° to render the silica insoluble, the subsequent procedure being as in the determination of silicon in iron. In this case, however, it is necessary to evaporate to dryness the liquid from which the silica has been removed by filtration and to heat the residue again at 135° to recover the small quantity of silica always remaining in solution. In the hydrochloric acid solution the manganese and phosphorus may be determined (*see* p. 196). In this case also it is well to test the purity of the silica obtained by treatment with hydrofluoric and sulphuric acids as on p. 171.

(*b*) FUSION WITH SODIUM CARBONATE AND MAGNESIA. 0·3–1 gram of the sample, very finely ground in an agate mortar, is mixed with about 10 parts of an intimate mixture of sodium carbonate (2 parts) and magnesium oxide (1 part), the mixture being placed in a fairly large platinum crucible, the bottom of which is covered with a thin layer of the sodium carbonate-

[1] The accuracy of the method has been confirmed also by Namias: *Ind. Chim. Miner. e Metall.*, 1915, II, p. 281.

magnesia mixture. The covered crucible is heated for about an hour in a good bunsen flame and then for about half an hour in a blowpipe flame.

When cold, the solid cake is placed in a porcelain dish, the crucible being washed first with water and then with hydrochloric acid, the latter being then gradually added until the ferric and magnesium oxides are completely dissolved (10 grams of the mixture require about 45 c.c. of HCl of D 1·12). The liquid is afterwards evaporated to dryness and treated further as in the preceding method.

**2. Determination of the Carbon.**—With products not attacked by acids, the carbon should be estimated by direct combustion in a current of oxygen (*see* Iron, 1, *b*).

**3. Determination of the Manganese.**—(*a*) The hydrochloric acid solution obtained in the determination of the silicon as under 1, *a* or 1, *b* is placed in a measuring flask. The residue remaining after treatment of the silica with hydrofluoric and sulphuric acids is dissolved in hydrochloric acid or, if insoluble matter then remains, fused with sodium carbonate and the fused mass dissolved in hydrochloric acid. This solution is added to the other in the measuring flask, the whole made up to volume and the manganese titrated by Volhard's method (*see* Ferro-manganese).

(*b*) In presence of chromium or vanadium, 0·2–2 grams of the sample are fused with a mixture of sodium carbonate and magnesium oxide (*see* 1, *b*) and the product lixiviated with hot water (if the mass is green owing to the presence of manganates, these are reduced by addition of a small quantity of sodium peroxide, excess of which is decomposed by boiling for some time). The residue is collected on a filter, washed with hot water, dissolved in conc. hydrochloric acid, boiled to expel chlorine, and, when cool, made up to volume in a 250 c.c. measuring flask: in an aliquot part the manganese is estimated by Volhard's method (*see* Ferro-manganese).

**4. Determination of the Phosphorus.**—(*a*) An aliquot part of the hydrochloric acid solution obtained after elimination of the silica (*see* 1, *a* and *b*) is concentrated to a syrup and the phosphorus precipitated with the molybdate reagent (*see* Determination of phosphorus in iron).

(*b*) 1-3 grams of the sample are fused with the sodium carbonate-magnesia mixture (*see* 1, *b*), the product being dissolved in hydrochloric acid and the silica rendered insoluble and removed. The solution is then evaporated to dryness, the residue dissolved in nitric acid and the phosphoric acid precipitated with the molybdate reagent.

**5. Determination of the Sulphur.**—1-3 grams of the sample are fused with sodium carbonate and magnesia (*see* 1, *b*), the mass taken up in bromine water, the bromine expelled by boiling, hydrochloric acid added to dissolve the ferric oxide and magnesia, the silica rendered insoluble, the residue taken up in dilute hydrochloric acid and, the silica having been removed, the sulphuric acid formed precipitated in the filtrate with barium chloride (*see* Gravimetric determination of sulphur in iron).

***

The more common, commercial ferro-silicons have the following percentages of silicon: 20/25, 25/30, 50/60, ·75 and 80/90; those with the higher proportions are the more valued.

As impurities, ferro-silicon contains small quantities of carbon, manganese, phosphorus, sulphur and, sometimes, calcium. Phosphorus is an injurious constituent, the maximum allowable limit being 0·15–0·2%. The mean percentage compositions of the commoner commercial forms are (Geiger) :

TABLE XV

**Compositions of Ferro-silicons**

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| Silicon | 25·89 | 29·66 | 51·80 | 53·75 | 51·20 | 75·67 |
| Iron | 72·92 | 72·99 | 47·30 | 45·09 | 48·89 | 23·01 |
| Carbon | 0·52 | — | 0·30 | 0·11 | — | 0·31 |
| Manganese | 0·42 | 0·56 | 0·35 | 0·11 | 0·37 | 0·26 |
| Sulphur | 0·03 | 0·01 | 0·02 | 0·005 | 0·007 | 0·01 |
| Phosphorus | 0·04 | 0·30 | 0·04 | 0·041 | 0·04 | 0·04 |
| Aluminium | — | 0·30 | — | 0·60 | 0·17 | — |
| Chromium | — | 0·25 | — | — | — | — |
| Copper | — | — | — | 0·04 | — | — |
| Lime | — | — | — | 0·05 | 0·21 | — |

## FERRO-MANGANESE AND SPIEGELEISEN

Ferro-manganese is usually obtained in the blast furnace from a mixture of iron and manganese minerals, and serves for the de-oxidation of steels and for the preparation of manganese steels and other special alloys. It is slightly yellowish white, compact and with a granular structure intersected, especially in the high percentage types, by bluish, iridescent, acicular crystals.

*Spiegeleisen* is a form of white cast-iron very rich in manganese with a peculiar lamellar structure and a shining and sometimes iridescent surface ; it has the same uses as ferro-manganese.

Analysis of these products may include, besides the determination of the manganese, also those of the carbon, silicon, phosphorus, sulphur, etc., which are always present in the commercial products in larger or smaller quantities.

**1. Determination of the Manganese.**—Numerous methods, gravimetric, volumetric and electrolytic, have been proposed for the determination of the manganese in ferro-manganese and manganiferous cast-irons in general. The following will be described : Volhard's volumetric method with the recent modifications introduced by Wolff, Schöffel and Donath, and the electrolytic method.

(*a*) VOLUMETRIC DETERMINATION. This method is based on the fact that, if a neutral solution of a manganese salt is treated with potassium permanganate, the whole of the manganese in it is oxidised at the expense of the permanganate and precipitated, together with that contained in the added permanganate, as the dioxide. The manganese present is calculated from the amount of permanganate necessary for the oxidation.

*Reagents.* (1) Potassium permanganate solution prepared by dissolving 3·2 grams of the pure salt in boiled distilled water and making up to 1 litre.

(2) Sodium arsenite solution, obtained by dissolving 1·6 gram of pure arsenious anhydride and 0·8 gram of pure sodium hydroxide in water, heating if necessary, and making up to 1 litre : 1 c.c. of this solution corresponds with about 0·5 c.c. of the permanganate solution.

*Titration of the permanganate solution* (Sörensen). About 0·3 gram of pure sodium oxalate, in minute crystals and dried at 100°, is weighed exactly, dissolved in 500–600 c.c. of boiling water, mixed with 50 c.c. of dilute sulphuric acid (1 vol. acid to 5 vols. water) and the permanganate solution run in from a burette until a faint pink colour persists. Since 670 grams of sodium oxalate are equivalent, as regards permanganate, to 164·79 grams of manganese as salt, the amount of manganese, $x$, corresponding with the permanganate used is given by

$$670{\cdot}0 : 164{\cdot}79 :: P : x,$$

where $P$ is the quantity of the oxalate taken. The quotient of $x$ by the number of c.c. of permanganate used gives the amount of manganese corresponding with 1 c.c. of permanganate.[1]

*Procedure.* 1–2 grams of ferro-manganese or 2–5 grams of spiegeleisen are treated with nitric acid (D = 1·18) according to the conditions described under 2 (p. 172). The solution is evaporated, ignited to decompose the nitrates, taken up in hydrochloric acid and the silica rendered insoluble, filtered and, if required, weighed. The hydrochloric acid solution, containing the manganese, when cold is made up to 250 or 500 c.c. in a measuring flask. The titration of the manganese is carried out on aliquot parts of the solution, each containing 0·04–0·08 gram of manganese.

If the sample is of high manganese content and hence contains too little iron, it is well to add to each portion 5–10 c.c. of ferric chloride solution (500 grams of pure ferric chloride dissolved in water acidified with hydrochloric acid and the volume made up to 1 litre). In this case it is necessary to ascertain, by a blank test under similar conditions, whether the ferric chloride absorbs permanganate and, if so, to allow for this in the calculation.

*Preliminary test.* Before titrating, a trial test must be made to establish the quantity of permanganate to be added.

An aliquot part of the solution is treated in a litre flask with a few drops of 30% hydrogen peroxide to oxidise any trace of ferrous salt and then heated to boiling to expel the excess of the oxidising agent. After 10–15 minutes' boiling, the volume is made up to 600–700 c.c. with boiling water, a suspension of zinc oxide[2] in water being then added in small amounts and with shaking until all the iron is precipitated in brown flocks (not pale

[1] The reaction between sodium oxalate and permanganate takes place thus: $5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5Na_2SO_4 + 10CO_2 + 8H_2O$, and that between a manganese salt and permanganate in the sense,

$$3MnCl_2 + 2KMnO_4 + 2H_2O = 2KCl + 5MnO_2 + 4HCl.$$

Hence 2 mols. of permanganate correspond with 5 of oxalate and with 3 of manganese salt, so that 5 mols. of oxalate (670·0) = 3Mn (164·79).

[2] Namias suggests that the zinc oxide be ground with sodium hypochlorite solution, left for some days and then washed several times by decantation (*Ind. Chim. Min. e Metall.*, 1915, II, p. 397).

brown, which would indicate too large an excess of the zinc oxide) and the supernatant liquid appears colourless.[1] The precipitate settles rapidly if the flask is held inclined in a suitable stand.

When the precipitate has deposited, 10 c.c. of the permanganate solution are added, the liquid shaken, the precipitate allowed to settle and, if the supernatant liquid is colourless, a further 10 c.c. of permanganate are added, this procedure being continued until the liquid contains excess of the reagent. The excess of permanganate is titrated with the sodium arsenite solution, which is added gradually and with shaking and with an interval after each addition until the liquid is decolorised. From the quantity of permanganate used, less that corresponding with the arsenite solution added (1 c.c. of arsenite = about 0·5 c.c. of permanganate), the amount of permanganate required to oxidise the manganese completely is calculated approximately.

*Titration.* For the actual titration of the manganese, an aliquot part of the liquid equal to that used in the preliminary test is oxidised with hydrogen peroxide, boiled, diluted with boiling water to 600–700 c.c. and zinc oxide added to precipitate the iron.

While the precipitate is settling, the volume of permanganate found necessary plus 3–4 c.c. is introduced into a beaker and then rapidly poured into the flask, the latter being shaken and the beaker rinsed out with water into the flask. When the precipitate has settled again, the excess of permanganate added is determined by titration with the sodium arsenite as in the preliminary test. Next, in order to determine the true titre of the arsenite with respect to the permanganate under the exact conditions used, a further volume of 5 c.c. of the permanganate is added and the liquid again decolorised by the arsenite solution. From these data a simple calculation gives the amount of permanganate required for the complete oxidation of the manganese, and hence the amount of the latter.

It is always advisable to carry out control determinations on different aliquot parts of the solution.

EXAMPLE. 1 c.c. of the permanganate solution is found to correspond with 0·00165 gram of manganese. In the actual test, 35 c.c. of permanganate were added and the excess required 8 c.c. of arsenite solution, of which 9 c.c. correspond with 5 c.c. of permanganate. Since

$$9 : 5 = 8 : 4{\cdot}44,$$

the amount of permanganate reduced will be $35-4{\cdot}44 = 30{\cdot}56$ c.c. and $30{\cdot}56 \times 0{\cdot}00165 =$ amount of manganese in the aliquot part of the solution taken.

Volhard's method is used more especially in laboratories where estimations of manganese are made regularly; it is fairly exact and, the solutions being ready, fairly rapid. It cannot be used directly in presence of chromium, vanadium and cobalt, these also reducing the permanganate (for the determination of manganese in presence of chromium, *see* p. 185). Further, to steels containing large proportions of nickel the method is not applicable, since the liquid remains greenish-yellow and the exact end of the reaction cannot be ascertained (for the determination of manganese in presence of large quantities of nickel, *see* p. 186). Many authors, instead of adding excess of permanganate and then

[1] It is necessary to add a slight excess of zinc oxide, but not a large excess, which may be harmful.

titrating the excess with sodium arsenite, prefer the simpler method of direct titration : the permanganate solution is added little by little to the boiling liquid and the precipitate allowed to settle after each addition, this being continued until the supernatant liquid exhibits a persistent pink colour. In this case, also, a preliminary trial titration is, of course, necessary. It appears, however, that under these conditions, intermediate oxides of manganese may be formed, so that the results are not always exact.

(*b*) ELECTROLYTIC DETERMINATION.[1]—1·5 gram of the finely powdered alloy is treated, in a covered porcelain beaker of about 100 c.c. capacity, with 30 c.c. of nitric acid (D 1·2) containing a few drops of hydrochloric acid. At the end of the action, the clock-glass and the edges of the beaker are washed with water, 1–2 grams of ammonium nitrate added and the liquid evaporated on a water-bath to a syrup and then carefully over a small direct flame to redness.

When cold, the oxides of iron and manganese are dissolved in 4–5 c.c. of conc. hydrochloric acid in the hot, 10 c.c. of 50% sulphuric acid being added to the cooled liquid and the solution heated on a sand-bath until the hydrochloric acid is completely expelled and copious white fumes appear. After being heated with water to dissolve the sulphates of iron and manganese, the liquid is filtered and the filtrate collected in a 250 c.c. measuring flask and the beaker and filter washed repeatedly with boiling water acidified with sulphuric acid.

The filter then contains the silica, contaminated by small quantities of graphitic carbon. If the silicon content is required, the procedure given on p. 171 is followed.

The liquid in the flask is made up to 250 c.c. and 50 c.c. (= 0·3 gram of the alloy) [2] treated in a 100 c.c. beaker with ammonia until the iron begins to precipitate. The liquid is then heated on a steam-bath and dilute sulphuric acid added drop by drop until the ferric hydroxide is completely dissolved. The solution of ferric and manganese sulphates is then poured into a solution of 6–7 grams of ammonium oxalate in a little boiling water contained in an electrolytic cell (not too narrow), 5–6 c.c. of 2% hydrazine sulphate solution being added and the liquid diluted to 200 c.c. and subjected to electrolysis to deposit the iron : $ND_{100} = 0{\cdot}7$ amp., voltage = 4–4·5, duration = 3–5 hours, Winkler electrodes (*see* later : Electrolytic analysis of metals).

When the electrolysis has commenced, 2% hydrazine sulphate solution is allowed to drop in the neighbourhood of the anode from a small tap-funnel drawn out to a capillary (8–10 drops per minute), this addition being continued uninterruptedly throughout the electrolysis.

As soon as the liquid loses its yellow tint and becomes completely colourless, a drop is removed, treated with a drop of dilute nitric acid, 2–3 c.c. of hydrochloric acid and as much ammonium thiocyanate solution. When only a barely perceptible pink coloration is thus obtained, the deposition of the iron may be regarded as complete.

[1] Belasio : "Separation of Iron from Manganese Electrolytically," *Ann. Labor. Chim. Gabelle*, 1912, VI, p. 207.

[2] With ferro-manganese containing much manganese, 25 c.c., corresponding with *0·15 gram* of the alloy, are taken.

Without interrupting the current, the cell is then lowered, the electrodes being washed as they emerge; the cathode is next detached and, if it is to be weighed, washed further with water and then with alcohol and dried at 70°.

The residual liquid is then heated—the anode, sometimes covered with manganese dioxide, being kept immersed—to destroy the ammonium carbonate formed by the decomposition of the ammonium oxalate, to redissolve the manganese dioxide, and to reduce the volume to 60–70 c.c. The liquid is then heated with 1·5 gram of chrome alum and 10 grams of ammonium acetate and the hot solution filtered directly into the matte Classen capsule. After 3 c.c. of ammonia (D 0·94) have been added, the liquid is mixed, brought to 70–80° and subjected to electrolysis, the capsule being connected with the positive pole. $ND_{100} = 0{\cdot}5–0{\cdot}6$ amp., voltage = 2–3, temperature = 70–80°, duration = about 2 hours.

When the deposition is found to be complete by raising slightly the level of the liquid, the disc functioning as cathode is lifted out and the contents of the dish poured away, the deposited manganese dioxide being carefully washed with water. The dish is then dried at 100° and heated at a dark-red heat to transform the dioxide and the higher oxides into the saline oxide, $Mn_3O_4$.

When cold, the dish is washed once more with water to remove any chromic acid which may be included, again ignited and weighed rapidly to prevent the manganese oxide from absorbing moisture: $Mn_3O_4 \times 0{\cdot}7205 = Mn$.

The electrolytic method certainly takes longer than the volumetric method, but has the advantage of not requiring standard solutions and of being applicable also in presence of chromium, cobalt, nickel and vanadium.

**2. Determination of the Carbon.**—This is usually carried out by the Corleis method (*see* Iron, 1, *a*) or, better, by direct combustion in a current of oxygen (*see* Iron, 1, *b*).

**3. Determination of the Silicon.**—When this is required, it may be effected along with the determination of the manganese (*see* Determination of silicon in iron, 2, *b*).

**4. Determination of the Phosphorus, Sulphur and Arsenic.**—These elements are estimated as in cast- or wrought-iron.

***

The manganese content of ferro-manganeses may vary from 25 to 85% and the carbon content from 5 to 7·5%, the two generally increasing together. Ferro-manganeses contain also 0·5–2·5% of silicon, small quantities of phosphorus (0·1–0·4%) and minimal traces of sulphur, copper, etc.

Spiegeleisen contains 0·2–1·2% of silicon, 4–5% of carbon and 5–25% of manganese, and sometimes, as impurities, small proportions of phosphorus and sulphur.

## SILICON FERRO-MANGANESE

### (Silico-spiegeleisen)

Silicon ferro-manganese may be regarded as a product intermediate to ferro-silicon and ferro-manganese. It is obtained in the blast furnace or the electric furnace, the latter yielding especially pure products. Its analysis includes the following:

**1. Determination of the Silicon.**—As silicon ferro-manganese is attacked either not at all or with difficulty by acids, the silicon should be estimated by the methods given for the determination of silicon in ferro-silicon.

**2. Determination of the Manganese.**—As in ferro-silicon.

**3. Determination of the Carbon.**—By direct combustion in a current of oxygen (*see* Iron, 1, *b*).

**4. Determination of the Phosphorus and Sulphur.**—As in ferro-silicon.

***

Silicon ferro-manganese obtained from the blast furnace contains about 20% Mn, 10–12% Si (occasionally 20%), 2–2·5% C, 0·01–0·2% P, and sometimes minimal traces of sulphur.

That from the electric furnace may contain 35–75% Mn, 20–35% Si, 0·6–1·5% C, 0·01–0·06% P, 0·02–0·03% S, and sometimes traces of copper, aluminium, etc.

## FERRO-CHROME

Ferro-chrome may be prepared in the blast furnace or the electric furnace and serves for making chrome steels. Its analysis includes:

**1. Determination of the Chromium.**—The sample is best attacked by the following methods.[1]

(*a*) Fusion with Sodium Hydroxide and Peroxide. 0·3–0·5 gram of the very finely powdered sample are mixed, in a silver crucible or dish and with a silver spatula, with 2 grams of sodium hydroxide in minute fragments, the mixture being covered with 4 grams of sodium peroxide and heated to incipient fusion, the flame being then removed to prevent the reaction from becoming too violent; the heat developed in the reaction rapidly melts all the contents of the dish or crucible. A little more sodium peroxide is added to the fused mass, the latter being heated gradually to fusion when the reaction begins to abate. After about 10 minutes, about 5 grams of sodium peroxide are mixed in and the mass heated rather more energetically so as to maintain it in a state of quiet fusion for 20–30 minutes, after which a further quantity of 5–6 grams of the peroxide is added and

[1] G. Gallo (*Rend. R. Accademia Lincei*, 1907, XVI, p. 58) proposes an ingenious method for attacking ferrous products with a high content of chromium. It consists in electrolysing at a temperature of 80–85° a 15% potassium chloride solution rendered slightly alkaline with potassium hydroxide, using as cathode a platinum wire and as anode the metal to be analysed. All the chromium in the latter is thus transformed into *alkaline* chromate.

the heating then continued for 20–30 minutes longer. If finely powdered, the sample should then be completely attacked.

(*b*) FUSION WITH SODIUM CARBONATE AND MAGNESIA. 0·3–0·5 gram of the finely powdered sample is mixed with about 10 parts of a mixture of sodium carbonate and magnesium oxide, and the mixture heated in a platinum crucible under the conditions prescribed for the analysis of ferro-silicon (1, *b*).

*Titration of the chromium.* The fused mass obtained by one of the above methods is lixiviated with water, as indicated on p. 183 (Chrome Steels), any manganates formed being reduced with sodium peroxide, the liquid filtered, boiled to expel excess of sodium peroxide and made up to volume in a 500 c.c. measuring flask ; the chromium is then titrated iodometrically on several 50 or 100 c.c. portions (*see* Chrome Steel).

If it is suspected that the attack of the metal has not been completed, the residue from the lixiviation is dried, fused with sodium carbonate and the fused mass again lixiviated, the resultant solution being added to that from the first treatment.

**2. Determination of the Carbon.**—This is effected by direct combustion in a current of oxygen (*see* Iron, 1, *b*).

**3. Determination of the Manganese.**—The residue obtained in the lixiviation with water of the fused mass is dissolved in hydrochloric acid and treated as indicated under Ferro-silicon, 3.

**4. Determination of the Silicon, Phosphorus and Sulphur.**—As in ferro-silicon.

***

Ferro-chrome contains 40–65% Cr (rarely 80%), quantities of carbon varying according to the degree of refining, and the ordinary impurities found in cast-iron. Three grades are distinguished commercially :

1. Refined ferro-chrome No. 1 (0·3–0·75% C, 60% Cr).
2. Refined ferro-chrome No. 2 (1–2% C, 60% Cr).
3. Ordinary ferro-chrome (4–10% C, 60% Cr).

The following table gives the mean compositions of various ferro-chromes (Bonini) :

TABLE XVI

**Composition of Ferro-chromes**

| Type. | Cr | Fe | C | Si | Al | Mn | Ca | S | P |
|---|---|---|---|---|---|---|---|---|---|
| 8–10% of carbon . | 54·50 | 22·00 | 9·50 | 2·25 | 0·80 | 0·15 | 0·25 | 0·04 | 0·03 |
| 7–8% ,, . | 63·50 | 21·50 | 7·50 | 5·30 | 0·80 | 0·16 | 0·25 | 0·04 | 0·03 |
| 5–6% ,, . | 64·00 | 28·50 | 5·50 | 0·40 | 0·50 | 0·15 | 0·25 | 0·04 | 0·02 |
| 3–4% ,, . | 64·00 | 31·00 | 3·50 | 0·40 | 0·40 | 0·15 | 0·30 | 0·04 | 0·02 |
| Less than 1% of carbon | 63·50 | 35·00 | 0·60 | 0·20 | 0·10 | 0·10 | 0·35 | 0·03 | 0·02 |

## FERRO-TUNGSTEN

Ferro-tungsten is obtained by the direct reduction of natural wolframite or scheelite with carbon in a crucible, or in the blast furnace or the electric furnace, and serves for the preparation of tungsten steels.

Ferro-tungsten and steels with high tungsten contents (20%) are insoluble or difficultly soluble in acids, and to attack them it is necessary to fuse with alkali. Their analysis includes:

**1. Determination of the Tungsten.**—0·5–2 grams of the finely powdered sample are fused with 10 parts of the mixture of sodium carbonate and magnesia, as under Ferro-silicon, 1 *b*, or 1 gram of the sample may be fused with 4–5 grams of sodium-potassium carbonate and 0·5 gram of potassium nitrate. In either case, the product is lixiviated with hot water, sodium peroxide being added and the liquid boiled to destroy the excess of this reagent, if the solution appears greenish owing to the presence of manganates. The liquid, which contains the tungsten as sodium tungstate, is filtered into a 500 c.c. measuring flask and the residue repeatedly washed, dried and again fused with sodium carbonate, the mass being lixiviated to recover any small amount of tungsten which may have resisted the first attack.

An aliquot part (50 or 100 c.c.) of the total solution is acidified with hydrochloric acid, evaporated to dryness, heated at 135°, taken up again in hydrochloric acid, etc., as described for the analysis of tungsten steel.

**2. Determination of the Carbon.**—With products insoluble in acid, direct oxidation in a current of oxygen must be employed (*see* Iron, 1, *b*).

**3. Determination of the Silicon.**—The procedure employed with ferro-silicon is followed, but since tungstic acid separates with the silica, the latter is treated with hydrofluoric acid and estimated by the loss in weight (*see* Tungsten Steels).

**4. Determination of the Manganese.**—This is carried out on the residue remaining undissolved when the fused mass is lixiviated with water (*see* Ferro-silicon, 3).

**5. Determination of the Phosphorus and Sulphur.**—As in ferro-silicon (*see* p. 196).

***

Crucible ferro-tungsten contains, on the average, 25–30% W, 60–70% Fe 1–1·5% C, with traces of manganese, phosphorus, etc.; that from the blast furnace always contains considerable proportions of manganese (in some types, up to 40%) and carbon (4–5%).

Ferro-tungsten obtained in the electric furnace usually has a high tungsten content (80–90% W, 10–20% Fe, very small amounts of carbon, silicon and manganese). Sometimes small quantities of calcium, magnesium, titanium, aluminium, nickel, molybdenum, vanadium, etc., are also found.

The mean percentage compositions of some of the ferro-tungstens prepared in the electric furnace are as follows (Bonini):

TABLE XVII

**Composition of Ferro-tungstens**

| No. | W | Fe | C | Si | Mn | Al | Sn | S | P |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 72·5 | 23·29 | 1·75 | 0·33 | 0·80 | 0·06 | — | 0·01 | 0·01 |
| 2 | 64·7 | — | 1·36 | 0·33 | 0·43 | 0·09 | Trace | 0·01 | 0·007 |
| 3 | 87·4 | — | 0·38 | 0·13 | — | — | Trace | 0·07 | 0·009 |
| 4 | 70·75 | 22·0 | — | 0·3 | 0·8 | — | — | 0·01 | 0·02 |
| 5 | 83·3 | 15·72 | 0·52 | 0·13 | — | — | — | 0·01 | 0·01 |

## FERRO-VANADIUM

Ferro-vanadium is obtained exclusively by electro-thermal processes, or by these in combination with alumino-thermal processes, from mixtures of ferric oxide and vanadium oxide. They serve as deoxidising agents in the refining of cast-iron and steels, and for the preparation of vanadium steels.

As prepared to-day it is comparatively pure and, besides iron and vanadium, usually contains only small quantities of carbon and silicon and sometimes traces of phosphorus and manganese. Its analysis includes:

**1. Determination of the Vanadium.**—1–2 grams of the sample are treated in a small porcelain dish with nitric acid (D 1·18), evaporated to dryness, calcined and the oxides obtained fused with sodium peroxide, the product being extracted with water as indicated in the analysis of vanadium steels.[1]

The liquids from the lixiviation are together made up to 500 c.c. and the vanadium in an aliquot part determined as with vanadium steel.

**2. Determination of the Carbon and Silicon.**—As in ordinary cast-iron.

**3. Determination of the Phosphorus.**—This is carried out on an aliquot part of the 500 c.c. (*see* 1, above) by the method given for estimating phosphorus in presence of vanadium (*see* Iron, 4, 3).

**4. Determination of the Manganese.**—As in ferro-silicon.

***

The usual types of ferro-vanadium contain 35–55% of vanadium, with small quantities of silicon (0·09–1·2%) and carbon (1–3%) and traces of phosphorus, sulphur, magnesium and aluminium.

The mean compositions of ferro-vanadiums made in the electric furnace are as follows (Bonini):

[1] If the sample can be finely powdered, it may be fused at once with a mixture of sodium carbonate and magnesia (*see* p. 195), the mass obtained being lixiviated with water.

TABLE XVIII

**Compositions of Ferro-vanadium**

| No. | V | Fe | C | Si | Al | Mn | Cu | S | P |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 55·0 | 40·00 | 4·00 | 0·30 | 0·10 | 0·30 | — | 0·03 | 0·04 |
| 2 | 52·8 | 45·84 | 1·04 | 0·09 | — | — | — | 0·025 | 0·02 |
| 3 | 47·4 | 51·20 | 1·07 | 0·09 | — | 0·07 | 0·01 | 0·009 | — |
| 4 | 34·1 | 64·22 | 1·42 | 0·12 | 0·12 | 0·12 | — | 0·03 | 0·009 |

## FERRO-MOLYBDENUM

This is obtained industrially by electro-thermal processes and is used essentially, together with chromo-molybdenum and molybdenum, for making molybdenum steels. The elements commonly estimated are molybdenum, carbon, silicon, manganese, phosphorus, sulphur and tungsten.

**1. Determination of the Molybdenum.**—1–2 grams of the finely powdered sample are heated at not too high a temperature with about 10 parts of the sodium carbonate and magnesia mixture, the semi-fused mass being extracted with hot water; these operations are then repeated to extract any small quantities of molybdenum remaining in the residue (*see* Chrome Steels). The two solutions together are made up to 500 c.c. in a measuring flask and the molybdenum in an aliquot part (50–100 c.c.) determined as in molybdenum steels.

**2. Determination of the Carbon.**—By direct combustion in a current of oxygen (*see* Iron, 1, *b*).

**3. Determination of the Silicon, Manganese, Phosphorus and Sulphur.**—As in ferro-silicon.

**4. Determination of the Tungsten.**—In an aliquot part of the 500 c.c. of solution (*see* 1, above) the tungsten is determined as in ferro-tungsten.

***

According to the character of the original ores, different types of ferro-molybdenum are obtained. These may contain 15–80% of molybdenum (usually 50–70%), from 0·5% (for the more refined products) to 5% of carbon, 0·1–0·5% of silicon and small quantities of manganese, sulphur, phosphorus, and sometimes tungsten.

The commoner commercial products have the following mean compositions (Guillet):

TABLE XIX

**Compositions of Ferro-molybdenum**

| Type. | Mo | C | Fe | Si | Al | S | P |
|---|---|---|---|---|---|---|---|
| Ordinary ferro-molybdenum | 53·30 | 1·87 | — | 0·17 | Trace | 0·03 | 0·03 |
| Refined ,, | 52·00 | 0·34 | — | 0·09 | — | 0·01 | 0·009 |
| Rich ,, | 84·80 | 2·27 | — | 0·11 | — | 0·02 | 0·007 |

## FERRO-TITANIUM

Ferro-titanium is prepared by electro-thermal and alumino-thermal processes from rutile and from iron ores rich in titanium, and serves as a deoxidising agent in the refining of cast-iron and steel.

**1. Determination of the Titanium.**[1]—0·5 gram of the finely powdered sample is heated in a platinum crucible and, after cooling, evaporated to dryness with a few c.c. of hydrofluoric acid. The residue is then heated for a short time in the same crucible with 5–7 grams of potassium bisulphate, the cooled mass taken up in hydrochloric acid (not too dilute) and heated on the water-bath until solution is complete. The liquid is made up to 500–600 c.c., mixed with 20–30 c.c. of concentrated sodium bisulphite solution and heated gently to reduce the iron to ferrous salts (a drop of the solution should give no appreciable colour with thiocyanate). When the reduction is complete and the temperature of the liquid not above about 40°, an addition is made, in one quantity and with shaking, of 70–100 c.c. of concentrated ammonia containing in solution 30 grams of potassium cyanide. The solution is then heated rapidly and kept near to the boiling point until the precipitate appears white and the supernatant liquid has assumed a greenish-yellow coloration. When cold, the liquid is filtered and the precipitate washed, first with ammoniacal ammonium sulphite solution and then with hot water. The moist precipitate is dissolved in hot, dilute hydrochloric acid and the titanium oxide in the clear solution precipitated by fresh addition of ammonia. The precipitate is filtered, washed, ignited strongly and weighed: $TiO_2 \times 0{\cdot}6005 = Ti$.

When aluminium occurs along with the titanium, the oxides thus separated are fused with bisulphate, the fused mass dissolved in hydrochloric acid and the titanium separated from the aluminium by means of cupferron.[2]

**2. Determination of the Carbon.**—By direct combustion in a current of oxygen[3] (*see* Iron, 1, *b*).

**3. Determination of the Silicon.**—0·3–1 gram is disintegrated with the mixture of sodium carbonate and magnesia (*see* Ferro-silicon, 1, *b*, p. 195). When cold, the semi-fused mass is moistened with water, ground in a mortar and poured into a beaker, the least possible quantity of rinsing water being used. The liquid is strongly acidified with hydrochloric acid —heating being avoided—left for 1–2 hours and then heated on a water-bath until the liquid becomes perfectly clear. The solution is evaporated in presence of sulphuric acid, heated until copious white fumes appear, diluted when cold and the separated silicon filtered off (*see* Ferro-silicon, 1, *b*).

**4. Determination of the Manganese, Phosphorus and Sulphur.**—As in ferro-silicon.

***

[1] Von Woldemar Trautmann (*Zeitschr. ang. Chem.*, 1911, p. 877; Boernemann and Schirrmeister (*Zeitschr. ang. Chem.*, 1911, p. 709).

[2] Bellucci and Grassi: *Gazz. Chim. Ital.*, 1913, i, p. 570.

[3] With products very rich in silica, disintegration in a current of chlorine must be employed.

In small quantities (0·2%) titanium is often found in ordinary cast-iron. The compositions of some of the commoner ferro-titaniums are as follows :

TABLE XX

**Composition of Ferro-titanium**

| No. | Fe | Ti | C | Si | Al | Mn | S | P |
|---|---|---|---|---|---|---|---|---|
| 1 | 36·85 | 56·63 | 4·62 | 1·25 | 0·44 | 0·10 | 0·045 | 0·02 |
| 2 | 78·54 | 18·37 | 0·67 | 1·40 | 0·69 | 0·18 | 0·074 | 0·024 |
| 3 | 87·68 | 11·21 | 0·67 | 0·37 | — | — | 0·03 | 0·04 |

## FERRO-ALUMINIUM

Ferro-aluminium is usually prepared in the electric furnace by reducing alumina in presence of iron, and serves, like metallic aluminium—which is much more used at the present time—as a deoxidising agent in the refining of cast-iron and steel. Its analysis includes :

**1. Determination of the Aluminium.**—Exact determination of the aluminium necessitates preliminary expulsion of the iron by exhaustion with ether in Rothe's apparatus, the aluminium being then precipitated as phosphate.[1] When, however, very exact determination is not required, the following more rapid method (Regelsberger's) may be followed.

5 grams of the coarsely powdered sample are dissolved in a porcelain dish in dilute sulphuric acid (1 : 4), evaporated to dryness and heated on a sand-bath until white fumes are emitted. When cold the sulphates are dissolved in hot water and the solution poured into a 300 c.c. measuring flask, cooled, made up to volume, and filtered through a dry pleated filter into a dry vessel.

To 100 c.c. of the filtrate sodium bisulphite or hyposulphite is added until the iron is completely reduced (a drop of the liquid should give no colour with thiocyanate), the liquid cooled, most of the free acid neutralised with sodium carbonate, and the solution poured into a boiling mixture of 50 c.c. of sodium hydroxide solution (containing 10 grams of sodium hydroxide) with 40 c.c. of potassium cyanide solution (containing 8 grams of potassium cyanide).[2] When cold, the liquid is introduced into a 500 c.c. measuring flask, made up to volume, and filtered through a dry filter. To 300 c.c. of the filtrate (= 1 gram of the alloy), concentrated ammonium nitrate solution (15 grams in a little water) is added, the liquid being boiled to expel most of the ammonia, and the precipitated aluminium hydroxide filtered off, washed until the washing water no longer gives a blue coloration with ferric chloride, dried, ignited and weighed : $Al_2O_3 \times 0{\cdot}5303 = Al$.

If the ammoniacal solution is heated too long, a little ferric hydroxide may be precipitated with the aluminium. In this case, the calcined and

[1] *See* A. Ledebur : *Leitfaden für Eisenhütten Laboratorien*, 9th edition, p. 153.

[2] If the reduction were not complete, small quantities of iron and manganese might be precipitated as hydroxides.

weighed alumina is finely powdered and treated with hydrochloric acid until it appears white, the iron reduced, without filtration, by means of zinc amalgam, and titrated with permanganate ; the corresponding amount of ferric oxide is deducted from the total weight of the alumina.

**2. Determination of the Carbon, Silicon, Manganese, Phosphorus and Sulphur.**—As with iron (*see* p. 163).

The more usual types of ferro-aluminium contain 10–20% of aluminium.

## ELECTROLYTIC ANALYSIS OF METALS

Analysis by the electrolytic method has now reached a high degree o perfection and forms a valuable aid in the examination of metals and alloys Owing to their accuracy, their simplicity and their neatness, electrolytic methods will be given the preference over other methods, and a brief description of the necessary apparatus and a short outline of the conditions to be observed in the various operations will now be given.

**1. Sources of Current.**—The continuous current used should not be very intense but must be as far as possible constant. It may be obtained from : *primary batteries*, *accumulators*, or the *street mains*.

Primary batteries do not answer very well the requirements of elec-

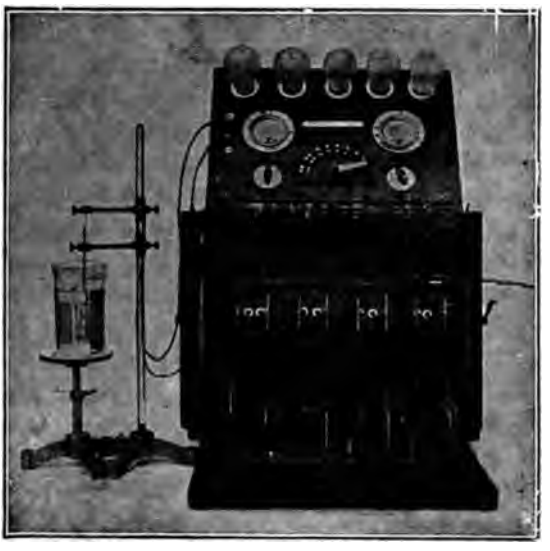

FIG. 16

trolytic analysis, since they usually yield a feeble current and must therefore consist of numerous cells, while they discharge rapidly and are therefore costly. The most suitable, owing to the constancy of the current produced, are : the *Daniell* cell and its modifications, and the *Cupron* cell. Also thermo-electric piles, although very delicate, may be usefully employed.

*Accumulators* are, however, very satisfactory, as regards both constancy of current and capacity, and they should be used in all plants of good

size. For analysis with stationary electrodes, a battery of 4 elements of 30–50 ampere-hour capacity is sufficient, whilst rotating electrodes may require 12 accumulators of this capacity. The various elements should connect with either a mercury or plug commutator, so that they may be grouped readily in parallel or in series or in mixed formation according to circumstances.

The *electricity supply current* may also be used and, if continuous, requires only the insertion of suitable resistances. If alternating, it must be converted into continuous current by an electrolytic rectifier, which serves particularly well when only low current intensities are required (1–1·5 amp.).

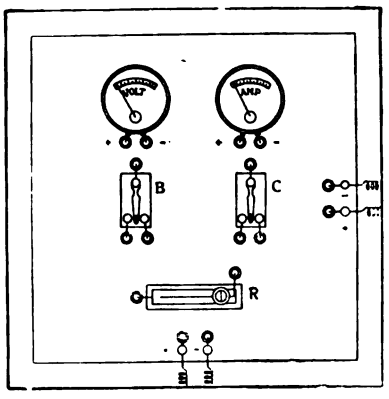

FIG. 17

Fig. 16 shows an electrolytic rectifier in connection with a small switchboard and the other arrangements necessary for electrolytic analysis.

**2. Distribution of the Current.**—The switchboard for distributing the current is very simple. It includes essentially a rheostat (Fig. 17, *R*) to regulate the current, an accurate amperemeter and voltmeter, a commutator *C* for inserting or cutting-out the amperemeter in the circuit including the electrolytic cell, and an interruptor *B* to insert at will the voltmeter and measure the pressure at the terminals. In any laboratory the current may be distributed in the form most convenient to the particular circumstances.

**3. Electrodes and Supports.**—In general the electrodes are of platinum or iridised platinum and that on which the metal is deposited, that is, the cathode, is of greater surface than the anode.

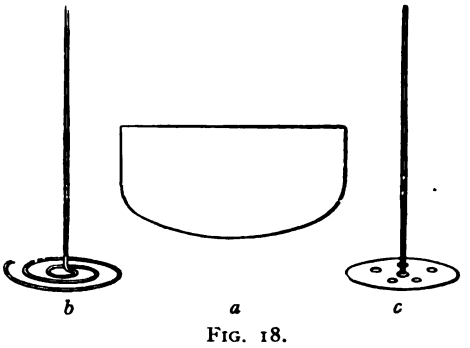

FIG. 18.

(*a*) WITH STATIONARY ELECTRODES. *Electrodes.* Of the numerous electrodes of different form and dimensions which have been suggested, those most suitable in practice are :

The *Classen dish*, with a smooth or matte surface (Fig. 18, *a*). This is a platinum dish of slightly convex base, weighing about 40 grams, holding about 200 c.c. and constituting the cathode. The anode is a disc of about 4·5 cm. in diameter with 5 holes, and supported by a stout platinum wire (Fig. 18, *c*) ; instead of this, a horizontal wire spiral may be used (Fig. 18, *b*).

*Winkler's gauze electrodes.* These are generally preferred because they weigh little (14–15 grams), permit perfect mixing of the liquid, are readily

washed and, what is of great practical importance, allow of the electrolysis of solutions varying in volume from 100 to 300–400 c.c. and of electrolysis in presence of precipitates. The cathode consists of an open cylinder 5 cm. high and 3–5 cm. in diameter, formed of iridised platinum gauze and supported by a thick platinum wire (Fig. 19, *a*). The anode forms a platinum wire spiral (Fig. 19, *b*).

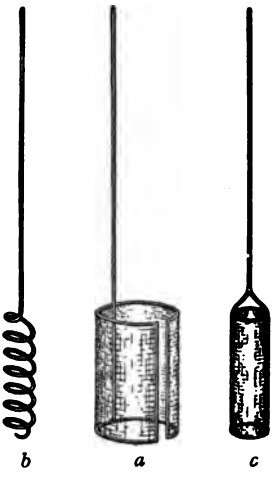

FIG. 19

In many cases, especially when copper and lead are being determined simultaneously, the Winkler spiral may be replaced with advantage by a small cylinder of iridised, matte platinum gauze,[1] 1·5 cm. in diameter and 5 cm. high (Fig. 19, *c*); on this as much as 0·3 gram of lead may be conveniently deposited as peroxide, whilst the copper is deposited on the cathode.

*Supports.* The most convenient and the most common are those of Classen. They consist of a heavy iron foot carrying a thick vertical glass rod. To the insulating rod are fixed by means of pressure screws, the electrode holders, those for Classen electrodes being a ring furnished with three platinum points on which the dish rests and a binding screw for suspending the anode, and those for Winkler electrodes two connecting screws (*see* Fig. 16).

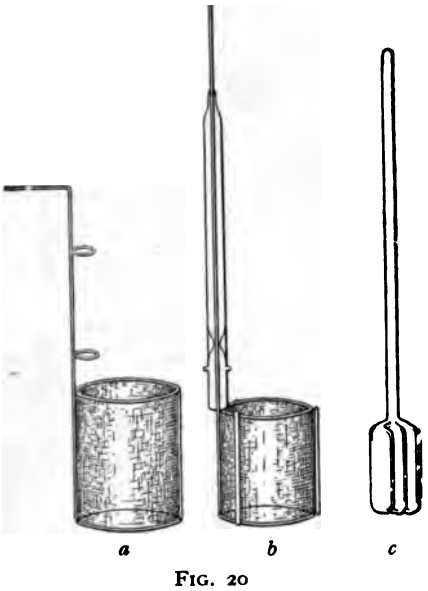

FIG. 20

(*b*) WITH ROTATING ELECTRODES. *Electrodes.* These may be: the Classen dish, within which the disc acting as anode revolves; or the Winkler cathode, inside which rotates a platinum spiral wound round a glass rod to give it solidity (Fig. 21). Other electrodes which are much in use and very convenient are those of Fischer, consisting of two concentric gauze cylinders (Fig. 20, *a*, *b*), insulated by quartz rods; the electrodes remain stationary, the liquid being kept in motion by a glass stirrer (Fig. 20, *c*) revolving inside the smaller cylinder.

*Stands.* These, besides supporting the electrodes, should permit of the rotation of one of the electrodes or of a stirrer. In its simplest form, a stand for rotating electrodes is shown in Fig. 21. One of the screws of the stand is replaced by a support carrying a rotating axis on which the

[1] Belasio: "Analysis of Bronzes for Ornamentation, so-called Nickel Bronzes" (*Rassegna mineraria*, 1909, XXXI, p. 50).

anode is fixed. The rotation may be imparted by a water turbine or an electric motor of adjustable speed. Much more perfect is the Fischer stand made for his electrodes and suitable also for use with the Classen dish (Fig. 22).

Another means for obtaining the rotation of the electrolyte is that pro-

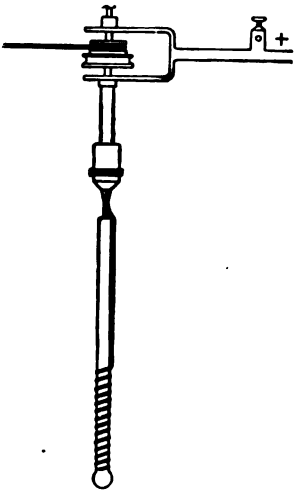

FIG. 21.

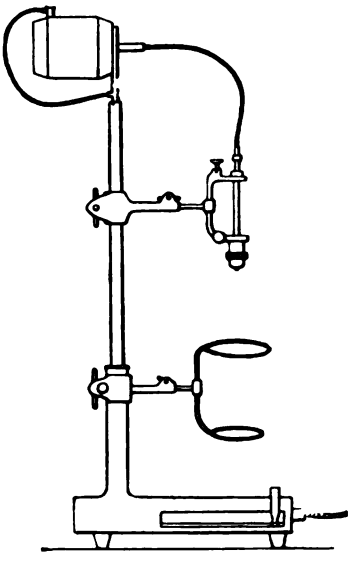

FIG. 22.

posed by Frary and based on the principle that any conductor carrying a current and situate in a magnetic field tends to move with a velocity depending on the intensities of the current and of the magnetic field. The arrangement of the apparatus is shown in Fig. 23. In practice, preference is given to mechanical methods of agitation.

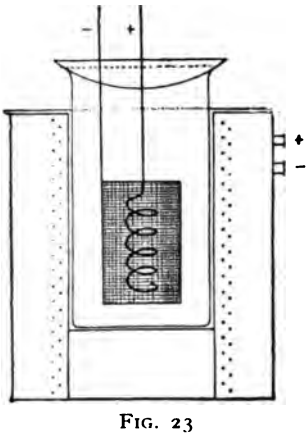

FIG. 23

**Practical Rules.**—When use is made of Winkler's electrodes, which are the most practical, the electrolysis is carried out in a beaker which is fairly tall and not too narrow. The prescribed reagents are added, suitably diluted so that the electrodes remain completely immersed, and mixed. The beaker is placed on a stand of adjustable height or on a tripod fitted with wire gauze if the electrolysis is to be carried out in the hot. The electrodes are then arranged, care being taken that the bottom of the cathode is about 1 cm. from the bottom of the beaker and that the anode is exactly in the middle of the gauze cylinder and almost touches the base of the beaker. The latter is then covered with a divided clock-glass with three semicircular gaps in each half, so that three circular holes are left to take the stems of the

electrodes and a thermometer, if this is required. The handle of the rheostat is placed to give the maximum resistance, the current started, the amperemeter and voltmeter inserted in the circuit, and the rheostat gradually regulated until the measuring instruments indicate the proper current and voltage; the instruments are then cut out.

With the Classen capsule the same directions are to be followed. The dish containing the electrolyte is placed on the proper stand, the anode arranged centrally and a few centimetres from the bottom, the cover fitted and so on, as above.

When rotating electrodes are used, the procedure is the same: when the electrodes are in place, the rotating apparatus is started so as to give the prescribed velocity (number of turns per minute), the cover fitted, the current regulated and the electrolysis continued.

**Detection of the End of the Deposition.**—When the prescribed time has elapsed, the deposition of the metal to be determined should be complete. To ascertain if this is so, two means are used: (1) If the deposited metal is different in colour from platinum (e.g., copper), the level of the electrolyte is raised a few millimetres by addition of water; if, after some time (15 minutes), the newly immersed part of the electrode shows no coating of the metal being determined, the deposition is complete. (2) A drop of the electrolyte is removed and tested for the metal by its most sensitive reactions.

**Washing of the Electrodes.**—With Winkler electrodes, the washing is very simple. The covers and thermometer are removed and washed with water, the beaker grasped in the left hand and the supporting stand removed without interrupting the current. The beaker is then rapidly but carefully lowered and replaced by a small beaker, which contains, according to circumstances, distilled water or water acidified with sulphuric acid and is supported on the stand. After 10–15 minutes the cathode is detached, washed by a gentle jet of distilled water, then with alcohol and finally with ether, dried in an oven at 60–70°, cooled in a desiccator and weighed.

With the Classen dish two cases present themselves. If the electrolyte has no energetic solvent action on the deposited metal, the covers are removed, the anode detached and placed in a beaker which is kept near, the dish being emptied into the same beaker and washed with a little water. The washing is then completed with water, alcohol and ether, and the dish dried at 60–70°, cooled in a desiccator and weighed. If, however, the electrolyte is acid, it may attack the metallic deposit during these manipulations; in this case, the washing should be carried out without interrupting the current. A small stream of distilled water is passed into the dish by means of a Marriotte's bottle or otherwise, while at the same time the liquid is drawn off, by a syphon reaching almost to the bottom of the dish, at such a rate that the level of the surface is always slightly above the deposited metal. This process is continued until the solution in the dish assumes a neutral reaction. The dish is then removed from its stand, washed with water, alcohol and ether, and dried at 60–70°.

With rotating electrodes, the same precautions are followed: at the

end of the electrolysis the current is lowered, the rotation stopped and the usual washing and drying of the cathode effected.

**Dissolution of the Metallic Deposits.**—Deposits of copper, zinc, nickel, silver, etc., are dissolved in nitric acid ; tin and iron in hydrochloric acid ; antimony in nitric acid containing a little tartaric acid in solution ; lead peroxide in nitric acid with a little oxalic acid dissolved in it ; manganous-manganic oxide in dilute sulphuric acid containing hydrogen peroxide. When Winkler electrodes are used, it is very convenient to immerse them in a tall, narrow vessel fitted with a ground stopper and containing the proper acid, which may be used repeatedly.

## COPPER AND ITS ALLOYS

The more important commercial products are : refined and electrolytic copper and its various alloys with phosphorus, silicon, manganese, zinc, tin and nickel.

After the usual tests for industrial copper, methods for the analysis of its principal alloys will be given, beginning with alloys of copper with phosphorus, silicon and manganese, and coming later to the most important ones, namely, the ordinary and special brasses and the ordinary and special bronzes.

Alloys of copper with nickel and zinc (argentan) will be treated along with nickel and its alloys, and its alloys with tin and antimony (anti-friction metals) along with tin and its alloys.

### COPPER

The complete analysis of commercial copper, that is, the determination of the copper and of all the extraneous elements accompanying it in large or small proportions (Bi, Pb, Sb, As, Sn, Ag, Au, Fe, Ni, Co, Zn, S, Se, Te, C, P, Si, O, etc.) is a very long and delicate operation.[1] Beyond a determination of the copper, commercial analyses as a rule require only estimations of the more injurious elements, especially of bismuth, arsenic, phosphorus, antimony, lead, sulphur, nickel, iron and oxygen. Rapid and exact methods for determining these elements will, therefore, be given.

**1. Determination of the Copper** (by *electrolysis*).—5 grams of the metal in fine turnings, freed from fat by means of ether and from traces of iron from the sampling tool by means of a magnet, are placed in a tall, narrow beaker covered with a clock-glass or with an inverted funnel of rather less diameter than the mouth of the beaker. The metal is there covered with water and treated with 5–7 c.c. of conc. sulphuric acid and 15–20 c.c. of nitric acid (D 1·33), gentle heat being applied towards the end of the action. Refined copper usually dissolves, but unrefined metal may leave a residue and traces of copper occluded in the latter must be extracted by boiling. In either case the unfiltered liquid is made up to

[1] See Hampe : *Chem. Zeit.*, 1893, XVII, p. 1678 ; Fresenius : *Quantitative Analysis* ; A. Hollard : *Chem. Zeit.*, 1900, XXIV, p. 146.

250–300 c.c. and electrolysed at the ordinary temperature with a current of 0·5–1 amp., using Winkler electrodes; duration, 12–15 hours.

When the deposition is complete (*see* p. 213), the electrolytic beaker is replaced, without interrupting the current, by another small beaker containing water faintly acidified with sulphuric acid, the cathode being detached after some time and washed first with water, then with alcohol, and lastly with ether; it is then dried at 70° and weighed. The increased weight represents copper and any silver present; the latter metal is determined as in 9 (below).[1]

If the copper deposited is not of a good, brilliant colour, but appears brownish and spotted (presence of arsenic or bismuth), it is redissolved in a mixture of 5–7 c.c. of conc. sulphuric acid and 15–20 c.c. of nitric acid (D 1·33), diluted to 250–300 c.c. and again electrolysed with addition of a little powdered lead sulphate (0·4 gram) and ferric sulphate (0·5 gram) to prevent traces of arsenic and bismuth from being deposited with the copper.

The residual liquid free from copper, together with the wash water, serves for the determination of antimony (*see* 5).

**2. Determination of the Bismuth.**[2]—(*a*) ELECTROLYTICALLY. 10 grams of the sample are dissolved in 50 c.c. of nitric acid (D 1·33), 10 c.c. of sulphuric acid being added when the action is complete and the solution evaporated to dryness. The residue is taken up in 200 c.c. of water containing 5 c.c. of sulphuric acid, the liquid being heated to boiling and the boiling liquid treated with 10 c.c. of phosphoric acid (D 1·71). When cold it is mixed with 30 c.c. of alcohol and, after 12 hours, filtered by decantation. The precipitate, which contains all the lead and bismuth of the sample, is washed first with a solution containing by volume about 1% of sulphuric acid, 5% of phosphoric acid and 15% of alcohol, and then with a dilute solution of ammonium sulphide and potassium cyanide [3] to remove the last traces of copper, arsenic, antimony, etc. The precipitate is then dissolved in the hot in nitric acid diluted with an equal volume of water, the liquid filtered by decantation and the residue treated with aqua regia diluted with an equal volume of water, filtered and washed with boiling water. The solution is evaporated with 12 c.c. of sulphuric acid until copious white fumes of sulphuric acid appear and, when cold, is treated

[1] In presence of large quantities of silver, the electrolysis should be started at 30° with a current of 0·1 amp. to deposit all the silver first. After some hours the current intensity is raised to 0·5–1 amp. and the electrolysis continued at the ordinary temperature until all the copper is deposited.

[2] *Detection* of bismuth in copper (Abel and Field).—About 6 grams of the sample are dissolved in nitric acid, treated with about 0·3 gram of lead nitrate dissolved in a little water, with ammonia until the reaction is alkaline and with a little ammonium carbonate. After standing a little while, the liquid is filtered, the precipitate washed with ammoniacal water and dissolved in hot acetic acid, and sufficient potassium iodide, dissolved in a little water, added to dissolve in the hot the precipitate at first formed. As it cools, the solution deposits lead iodide crystals which, instead of pale yellow, are orange or red in presence of bismuth. By this method, 0·02 m. grm. of bismuth is detectable. A blank experiment with pure lead nitrate should be made and the colour of the lead iodide compared with that obtained in presence of the copper.

[3] 100 c.c. of this solution should contain 5 grams of potassium cyanide and 5 c.c. of ammonium sulphide prepared by saturation of 10% ammonia with hydrogen sulphide.

with about 100 c.c. of water containing a little alcohol. The liquid is filtered, the filter washed with water acidified with sulphuric acid and containing alcohol (in all 35 c.c. of alcohol should be used) and the liquid, about 300 c.c. in volume, electrolysed to determine the bismuth.[1] $ND_{100}$, i.e., current per 100 sq. cm. of electrode surface, = 0·1 amp.; duration = about 48 hours; maximum quantity of bismuth which can be deposited = 0·1 gram.

(*b*) GRAVIMETRICALLY.[2] 10 grams of the sample are dissolved in 60 c.c. of nitric acid (D 1·3) and the excess of acid expelled by evaporation on a water-bath. The residue is dissolved in 400 c.c. of water and neutralised, with continual shaking, by means of a very dilute solution of sodium hydroxide. As the acidity diminishes, more and more dilute alkali should be used in order to prevent separation of large clots of copper hydroxide. A slight excess of the alkali is added so as to produce a faint permanent turbidity, the liquid being made up to a litre and heated for an hour on the water-bath, a few drops of the alkali solution being added should the turbidity tend to disappear. A little further sodium hydroxide solution is then added to form a just perceptible precipitate and, after 15–20 hours, the precipitate—containing, besides copper, all the bismuth, iron, etc., of the sample—is collected on a filter, washed with cold water and dissolved in hot dilute hydrochloric acid. The bismuth is precipitated by rendering alkaline with ammonia, the excess of which is expelled on the water-bath (the copper should not precipitate), and the precipitate filtered off and washed with hot water. The precipitated bismuth hydroxide is redissolved in hydrochloric acid, the liquid diluted and precipitated with hydrogen sulphide, the precipitate filtered off and washed with yellow ammonium sulphide to dissolve any traces of antimony present and then with water. The bismuth sulphide is then dissolved in nitric acid and reprecipitated with ammonia, the precipitate filtered off, washed, dissolved in nitric acid and the solution evaporated in a tared porcelain crucible, the bismuth oxide being gently heated and weighed: $Bi_2O_3 \times 0{\cdot}8965 = Bi$.

**3. Determination of the Arsenic.**—5 grams of the sample[3] in fine borings are introduced into the flask used for arsenic distillation (*see* Iron, 6) and are gently shaken while 100–125 c.c. of conc. hydrochloric acid containing in solution 50 grams of ferric chloride free from arsenic[4] are added through a long-stemmed funnel. The flask is closed with the stopper carrying the pressure-regulating apparatus, connected with the pipette dipping into the ammonia solution, and heated gently to dissolve the metal completely; the flame is then increased and distillation carried on until the ammoniacal solution becomes faintly acid. At this point the distillation is suspended, the pipette removed and washed, and the arsenic determined iodometrically as indicated on p. 179.

[1] The lead sulphate which separates, dissolved in nitric acid containing a little ammonium nitrate and copper nitrate (67 c.c. of nitric acid of D 1·33, 40 c.c. of ammonia of D 0·923 and 2–3 grams of copper nitrate), may be electrolysed to determine the leap (*see* 6).

[2] Lunge: *Technical Methods of Chemical Analysis* (London, 1911), Vol. II, p. 199.

[3] With highly arsenical copper, smaller quantities (1–2 grams) are used and 10 grams of ferric chloride are dissolved in the hydrochloric acid per gram of metal taken.

[4] The purity of the reagents is ascertained by a blank test.

**4. Determination of the Phosphorus.**—10–20 grams of the sample are dissolved in nitric acid, the excess of the latter expelled, and the liquid treated with 1 c.c. of ferric chloride solution free from phosphorus and rendered alkaline with ammonia. The precipitate is filtered off, washed and dissolved in hydrochloric acid, and the acid solution treated as described on p. 174 or, if in presence of arsenic, on p. 176.

**5. Determination of the Antimony** (Classen).—The solution from which the copper has been removed electrolytically as in 1, together with the washing water from the small beaker, is evaporated until the nitric acid is completely expelled; if the anode is brown, it is kept immersed for some time, a few drops of hydrogen peroxide being added to dissolve the peroxides deposited on it.[1] The solution is diluted with water and subjected to the action of hydrogen sulphide in the cold to prevent the precipitation of the arsenic. The precipitate is filtered off and washed, and the antimony oxide and sulphide and any tin oxide and sulphide dissolved in 80 c.c. of sodium sulphide solution (D 1·225), 4–5 grams of potassium cyanide being added to the solution and the latter electrolysed in the Classen dish. $ND_{100} = 0{\cdot}15$ amp.; duration = 10–15 hours.

**6. Determination of the Lead** (by *electrolysis*).—5 grams of the sample are treated with 20–30 c.c. of nitric acid (D 1·18), the nitrous fumes expelled by boiling and the liquid diluted to 250–300 c.c. and electrolysed, with a Winkler cathode and a tared gauze cylinder anode, as described on p. 210. $ND_{100} = 0{\cdot}5$–1 amp., duration = 10–15 hours.

Whilst copper is deposited on the cathode, lead is deposited as peroxide on the anode. At the end of the electrolysis, the electrodes are removed and washed with water, and the anode, after further washing with distilled water, dried at 180–200°, cooled and weighed: $PbO_2 \times 0{\cdot}866 = Pb$.

If manganese and considerable quantities of bismuth and iron are present, small amounts of the oxides of these metals are deposited on the anode with the lead peroxide. In such case the deposit is dissolved in nitric acid containing a little alcohol, the solution being evaporated with sulphuric acid until copious white fumes appear, the residue being taken up in water, a little alcohol added, and the lead sulphate separated and weighed. Another method consists in employing, for the determination of the lead, the lead sulphate which separates during the necessary procedure for the electrolytic determination of the bismuth (*see* 2, *a*).

**7. Determination of the Sulphur.**—The solution freed from copper and lead by electrolysis (*see* 6) is evaporated to dryness (to fix the sulphuric acid it is advisable to add a little sodium carbonate). The residue is taken up twice in hydrochloric acid, the liquid being evaporated to dryness each time to expel the whole of the nitric acid. The final residue is then dissolved in 5 c.c. of conc. hydrochloric acid and 50 c.c. of hot water and barium chloride added to the clear liquid thus obtained to precipitate the sulphuric acid formed by oxidation of the sulphur during the attack of the metal, the ordinary conditions being observed.

**8. Determination of the Iron, Nickel and Zinc.**—5 grams of

[1] In case the copper has been deposited twice, the solution from the second deposition must also be added.

the sample are treated with 5–6 c.c. of sulphuric acid and 15–20 c.c. of nitric acid, the liquid being diluted to 250–300 c.c. and electrolysed to eliminate the copper (*see* 1). The electrodes are then removed and washed with water, and the solution evaporated until the nitric acid is completely expelled. If the anode appears brown, it is left for some time immersed in the evaporating liquid, the peroxides deposited on it being caused to dissolve by addition of a few drops of hydrogen peroxide. When cold the residue is dissolved in water and the solution treated in the hot with hydrogen sulphide to precipitate the arsenic, lead, antimony, etc. The precipitate is filtered off and washed, and the filtrate boiled to expel the hydrogen sulphide, treated with 1–2 c.c. of hydrogen peroxide, boiled and rendered alkaline with ammonia to precipitate the iron. When considerable quantities of iron are present, it is advisable to repeat this precipitation after solution of the precipitate in a little hot, dilute sulphuric acid. The ferric hydroxide separated is washed, dried and ignited; it may be weighed directly or dissolved in a little dilute sulphuric acid and estimated electrolytically (*see* p. 200).

The filtrate, or the mixed filtrates from the two precipitations, are used for the electrolytic determination of the nickel and zinc. First, 30–40 c.c. of ammonia and a few crystals of hydroxylamine sulphate are added and the nickel then deposited, the zinc being determined in the residual solution (*see* Analysis of Argentan).

When determination of the zinc is not required, the nickel may be precipitated directly in the iron-free alkaline solution by alcoholic dimethylglyoxime solution (*see* Gravimetric Analysis of Argentan).

**9. Determination of the Silver.**—2·5 grams of the sample are dissolved in 100 c.c. of nitric acid diluted with an equal volume of water, the solution being boiled to expel nitrous vapours and, without filtering, heated to 95° and treated with a few drops of hydrochloric acid to precipitate the silver. The liquid is heated on the water-bath to separate the precipitate, which is filtered off and washed with hot water, the silver being determined in this impure silver chloride either electrolytically or gravimetrically.

(*a*) ELECTROLYTIC METHOD. The precipitate is dissolved in the hot in 120 c.c. of 10% potassium cyanide solution, then diluted to 300 c.c. and electrolysed with a current of 0·1 ampere.

(*b*) GRAVIMETRIC METHOD. The silver chloride is dissolved in ammonia by digestion in the hot for some time, the solution being filtered and acidified with nitric acid to reprecipitate the silver chloride, which is weighed as usual.

**10. Determination of the Total Oxygen.**—The oxygen present in commercial copper occurs largely as cuprous oxide and partly in combination with extraneous metals. It is determined by causing it to combine with hydrogen at a high temperature and estimating the water formed. A condition essential to accuracy is that the hydrogen must be perfectly dry and free from oxygen.

The hydrogen, made in a Kipp apparatus from pure zinc and dilute sulphuric acid, is purified by passing it successively through alkaline pyrogallol, permanganate solution and conc. sulphuric acid. Any traces of

oxygen still present are eliminated by passing the gas through a glass or porcelain tube containing platinised asbestos heated to redness, the water formed being absorbed by means of a U-tube charged with phosphoric anhydride.

Prior to the determination, a blank test is made, the hydrogen being passed through the glass or porcelain tube to be used in the determination and arranged on a combustion furnace; after about 10 minutes, a tared phosphoric anhydride tube, full of hydrogen and connected with a calcium chloride tube to keep atmospheric moisture away, is attached, the tube being then heated to redness and the stream of hydrogen continued for about an hour. At the end of this time the burners are extinguished and the tube allowed to cool in the current of hydrogen; the U-tube should exhibit no appreciable increase in weight.

For the determination, 10 grams of the sample, freed from grease and any traces of iron (*see* 1) are weighed in a perfectly dry porcelain boat, which is placed in the *cold, dry* combustion tube, the air being then expelled by passing hydrogen for 10–15 minutes. The phosphoric anhydride tube and its calcium chloride tube are then attached and the tube heated strongly near the boat for 20–30 minutes.

When the reduction is complete, the tube is allowed to cool in the current of hydrogen and the phosphoric anhydride tube weighed; the increased weight represents water, and this should correspond with the oxygen lost from the metal in the boat.

The determination of oxygen in copper is a very delicate and perhaps not quite exact operation. Metallographic examination gives information in this respect.

***

Copper of good quality should be bright red and very ductile and malleable; its fracture should be finely granular, of uniform colour and free from spots; its specific gravity should lie between 8·65 and 8·93, and it should contain more than 99·5% Cu (electrolytic copper may contain 99·8–99·9% or even more). As the purity diminishes, the specific gravity, malleability and ductility decrease.

Of the likely impurities, those of special influence on the mechanical properties are bismuth, lead, antimony, sulphur, arsenic, phosphorus, nickel, iron and oxygen.

According to Hampe, the presence of 0·02% Bi is sufficient to render copper brittle in the hot, while 0·05% makes it brittle also in the cold. Keller states that copper containing a few thousandths of bismuth is unsuitable for electrical conductors; a similar effect is exerted by lead in the proportion of 0·3–0·4%. Antimony was once regarded as highly injurious, but less than 0·5% appears innocuous; in whatever proportion, it lowers the electrical conductivity, and copper containing antimony is unfit for making brass. Sulphur, which may be present as cuprous sulphide, renders it cold short if present in greater quantity than 0·5%. On the other hand, phosphorus and arsenic in small proportions (not more than 0·5%) make it more tenacious and resistant, because they impede the formation of cuprous oxide, 0·5% of which greatly diminishes the tenacity and ductility (some types of copper may contain even more, electrolytic copper according to Keller, as much as 0·6–0·8%). On this account, certain railway companies use for their locomotive boilers copper containing not less than 0·2–0·3% of arsenic. Small proportions of iron and nickel may often be found in

TABLE XXI

## Compositions of Commercial Copper

| Source. | Cu | Bi | As | Sb | Pb | Fe | Ni + Co | Ag | O |
|---|---|---|---|---|---|---|---|---|---|
| Lake Superior (6 samples). | 99·74–99·96 | 0·0–0·1 | 0·009–0·037 | 0·0–0·088 | 0–trace | trace–0·008 | 0·0–0·012 | 0·027–0·112 | — |
| Mansfield (4 samples) . . | 99·19–99·51 | — | 0·025–0·061 | — | 0·006–0·206 | trace–0·037 | 0·279–0·467 | 0·014–0·028 | — |
| Oker (1 sample) . . . | 99·325 | 0·052 | 0·130 | 0·095 | 0·061 | 0·063 | 0·076 | 0·072 | 0·1166 |
| Chili (6 samples) . . . | 97·66–99·91 | trace–0·53 | 0·009–0·094 | 0·00–0·102 | 0·0–0·042 | trace–1·248 | 0·005–0·413 | 0·009–0·084 | — |
| Japan (8 samples) . . . | 98·22–99·80 | 0·0–0·003 | 0·009–0·077 | trace–0·088 | 0·0–0·05 | 0·006–0·038 | 0·02–0·08 | 0·014–0·113 | — |
| *Electrolytic coppers* | | | | | | | | | |
| Australia (Cobar) . . . | 99·947 | 0·004 | 0·008 | 0·026 | — | 0·006 | 0·009 | — | — |
| Japan (Mitsu-Bishi) . . | 99·983 | trace | — | 0·012 | — | trace | — | — | — |
| America (Electro-Montana) | 99·835 | — | — | 0·010 | trace | 0·004 | 0·007 | — | — |
| Do. (Keller) . . . | 99·989[1] | — | 0·00022 | 0·00065 | — | — | — | 0·00005 | 0·01 |
| Do. (Keller) . . . | 99·910[1] | 0·0017 | 0·01040 | 0·02730 | trace | — | — | 0·00004 | 0·05 |

[1] By difference.

commercial copper and do not modify its properties appreciably, provided their amount does not exceed 0·3–0·4%.

Compositions of the commoner commercial coppers are given in Table XXI (Hollard, Schnabel, Hampe).

## PHOSPHOR-COPPER

Phosphor-copper is usually employed as a deoxidiser and for the preparation of phosphor bronzes. It occurs mostly in cakes of metallic appearance and bronze or steel-grey colour and sometimes with bluish reflections; it is brittle and has a crystalline structure.

Its analysis comprises essentially determinations of the phosphorus and copper. The impurities, derived from those of the copper used in its preparation, may be estimated by the methods given on p. 214 for the analysis of commercial copper.

**1. Determination of the Phosphorus.**—0·5 gram of the finely powdered sample are treated in a covered dish with 10 c.c. of nitric acid (D 1·4), gentle heat being applied when the action slackens. If any unattacked metal remains after about 30 minutes, a few drops of hydrochloric acid are occasionally added and the liquid heated until solution is complete and then evaporated to dryness with 10 c.c. of nitric acid. The residue is extracted with hot water acidified with nitric acid and the liquid filtered to separate (and determine, if necessary) any traces of silica present, the filtrate being made up to 250 c.c.

50 c.c. of this solution are evaporated to 10 c.c. and treated with 150 c.c. of ammonium molybdate solution, the remaining procedure being as in the determination of phosphorus in iron (*q.v.*).

**2. Determination of the Copper.**—1 gram of the sample is treated with 10 c.c. of nitric acid (D 1·2) and 5 c.c. of hydrochloric acid in a covered beaker. The solution is evaporated with 2–3 c.c. of sulphuric acid until the nitric and hydrochloric acids are completely expelled and then heated on a sand-bath until white fumes of sulphuric acid appear. When cool the residue is taken up in hot water, the solution being mixed with 5–6 c.c. of nitric acid (D 1·4), made up to 200–250 c.c. and electrolysed (*see* p. 214): Winkler electrodes; $ND_{100} = 0{\cdot}3–0{\cdot}4$ amp.; duration = 10–15 hours.

Phosphor-copper usually contains 9–15% P (sometimes, however, only 0·5–5%). Preference is given in practice to products with 10% P.

## CUPRO-SILICON

Cupro-silicon or copper silicide, also improperly termed silicon bronze, is prepared in the electric furnace by reducing silica with carbon in presence of copper. It is used especially for the deoxidation of brasses and bronzes and for the preparation of copper-silicon alloys containing small quantities of silicon and used in electro-technics for telephone wires, cables, etc. (alloys with 0·2–3·5% Si).

Its analysis comprises essentially determinations of the silicon and

copper ; the impurities may, if required, be estimated as in commercial copper (*see* p. 215).

**1. Determination of the Silicon.**—1 gram of the finely powdered sample is treated with 10–20 c.c. of nitric acid (D 1·4) and heated for a long time. After addition of 1–2 c.c. of hydrochloric acid, it is again heated for a short time and finally evaporated in presence of 2 c.c. of sulphuric acid. The heating is continued on a sand-bath until copious white fumes of sulphuric acid are emitted, the cooled residue being treated with hot water, filtered, and the filter thoroughly washed with hot water acidified with sulphuric acid. The filter, still somewhat moist, is placed point upwards in a platinum crucible and the latter covered and heated, at first gently and later to ignition, the subsequent procedure being that followed in estimating silicon in iron or steel (*see* p. 171).

**2. Determination of the Copper.**—The filtrate from the silica is acidified with 5–6 c.c. of nitric acid, made up to 250–300 c.c. and electrolysed to determine the copper. Winkler electrodes ; $ND_{100} = 0{\cdot}3–0{\cdot}4$ amp. ; duration, 10–15 hours.

The commoner commercial types of cupro-silicon contain 10, 15, 20 and 35% of silicon.

## CUPRO-MANGANESE

The copper-manganese alloys are used as deoxidisers of copper, and for the preparation of copper-manganese alloys with a low content of manganese—so-called manganese bronzes—and of the manganese brasses and true manganese bronzes. Analysis includes determination of the copper and manganese and, sometimes, of the impurities, particularly the silicon, lead, iron and nickel.

**1. Determination of the Copper.**—1 gram of the sample is treated in a covered dish with 10–15 c.c. of nitric acid (D 1·2), 6 c.c. of dilute sulphuric acid (1 vol. acid to 1 vol. water) being added when the action is complete and the liquid evaporated on a water-bath to eliminate the nitric acid and then heated on a sand-bath until copious white fumes of sulphuric acid appear. When cool, the residue is stirred and gently heated with 30 c.c. of water to dissolve the copper and manganese sulphates, 5 c.c. of 95% alcohol being added and the mixture left for one or two hours. Any insoluble residue, consisting usually of silica and lead sulphate, is filtered off and washed with a mixture of 60 c.c. of water, 10 c.c. of alcohol and 0·5 c.c. of sulphuric acid, the filtrate being evaporated almost to dryness to expel all the alcohol, and the residue taken up in water, diluted to 150 c.c., heated to 60–70° and electrolysed to determine the copper : Winkler electrodes ; temperature = 60–70° ; $ND_{100} = 0{\cdot}2–0{\cdot}3$ amp. ; duration = 6-7 hours.

When the whole of the copper is deposited the solution is allowed to cool a little, the cover-glasses removed from the beaker, the latter slowly lowered and the electrodes washed with water as they emerge. The cathode is then washed with water, alcohol and ether, dried at 70° and weighed.

**2. Determination of the Iron and Manganese.**—The liquid from which the copper has been removed is treated with 2–3 drops of hydrogen peroxide, the anode being kept immersed to dissolve the coating of manganese dioxide. The liquid is boiled for a few moments, the electrode withdrawn and washed with water and the solution, when cold, made up to volume in a 300 c.c. flask. In aliquot parts the iron and manganese are determined either volumetrically or electrolytically.

(*a*) VOLUMETRIC METHOD. In 50 or 100 c.c. the iron is determined by titration with permanganate after reduction with amalgamated zinc.[1] In another aliquot part (50 or 100 c.c. according to the amount of manganese present), the manganese is titrated by Volhard's volumetric method (*see* Ferro-manganese).

(*b*) ELECTROLYTIC METHOD. In 100–200 c.c., according to the amount of manganese present, the iron and manganese are estimated as described for ferro-manganese.

**3. Determination of the Nickel.**—In an aliquot part of the 300 c.c. of solution (*see* 2), the nickel is determined by means of dimethylglyoxime in presence of the necessary quantity of tartaric acid (*see* Nickel Steel).

**4. Determination of the Silicon and Lead.**—The residue remaining on the filter when the copper and manganese sulphates are taken up in water (*see* 1) contains all the silicon and lead of the sample as silica and lead sulphate. The latter is now dissolved in nitric acid containing ammonium nitrate and the lead in the solution determined electrolytically in presence of copper nitrate (*see* Lead-tin Alloys).

The residue insoluble in nitric acid and ammonium nitrate consists of silica (possibly impure) and is filtered off, washed, ignited in a platinum crucible, weighed, treated with hydrofluoric acid and again weighed; the loss in weight represents silica (*see* Determination of Silicon in Iron).

With copper-manganese alloys containing little manganese (manganese bronzes) it is advisable to determine the copper separately in two distinct portions (1 gram each) of the sample. When the copper is eliminated, the two portions of manganese dioxide on the anodes are dissolved and made up together to 300 c.c.

***

Copper-manganese alloys contain about 25–30% of manganese with small quantities of iron, silicon, etc. Two principal types are met with commercially: the so-called impure alloy with 72–74% Cu, 23–24% Mn, 2·5–4·5% Fe and 0·2–0·5% Si, and the pure alloy with 70–72% Cu, 28–30% Mn, 0·1–0·3% Fe and 0·05–0·1% Si.

The alloys with a low manganese content or *manganese bronzes*, used, owing to strength in the hot, for valves, tie-rods for locomotives, etc., contain on the average 4–6% Mn and such impurities as are usually met with in commercial copper.

[1] This may be prepared by dissolving 5 grams of mercury in 25 c.c. of nitric acid (D 1·2), making the solution up to about 250 c.c., and immersing 500 grams of zinc in granules of about 1 mm. diameter in it for 2–3 minutes with continual agitation.

## ORDINARY BRASSES

Ordinary brasses are alloys of copper and zinc in various proportions always containing as impurities small quantities of lead, iron, tin and sometimes nickel, arsenic, sulphur, phosphorus and bismuth. Their analysis comprises the determination, by electrolytic or gravimetric methods, of the constituent elements and impurities.

### *A.* Electrolytic Methods

In a covered beaker, tall and narrow, 1 gram of the alloy in turnings or filings is dissolved at a gentle heat in 15 c.c. of nitric acid (D 1·2).

**1. Determination of the Tin.**—The solution is diluted with 30–40 c.c. of water and if it appears turbid owing to the presence of metastannic acid, it is evaporated to dryness, taken up in a few drops of nitric acid and a little water, heated for some time and filtered, the insoluble residue being collected on a small, tight filter and the filtrate in a 350 c.c. electrolytic beaker. The filter is washed, first with water faintly acidified with nitric acid and then with water alone, dried, ignited in a porcelain crucible and weighed [1]: $SnO_2 \times 0{\cdot}7881 = Sn$.

**2. Determination of the Copper and Lead.**—The liquid freed from the metastannic acid is treated with 15 c.c. of nitric acid of D 1·2 (in absence of tin, it is not necessary to add fresh acid, since the evaporation of the solution to dryness is omitted), made up to about 200 c.c., allowed to cool and electrolysed to determine simultaneously the copper and the lead [2]: Winkler cathode and matte gauze cylinder anode; $ND_{100} = 0{\cdot}3$ amp.; voltage, 1·8–2; duration, 10–15 hours. After half an hour or an hour, when the greater part of the lead has been deposited as peroxide on the anode, 20 c.c. of 10% sulphuric acid are added to the electrolyte, which is carefully stirred by means of a glass rod.

When the deposition of the copper and lead is complete, the electrolytic beaker is replaced, rapidly and without interruption of the current, by a small, tall and narrow beaker containing water acidified with sulphuric acid, this being replaced after some time by another beaker containing distilled water. Finally the electrodes are detached and washed, the cathode with water, alcohol and ether, followed by drying at 70°, and the anode with water alone, followed by drying at 180–200°: $PbO_2 \times 0{\cdot}866 = Pb$.

**3. Determination of the Iron and Zinc.**—The liquid from which the copper and lead have been separated and the wash water from the first beaker are evaporated together until white fumes of sulphuric acid are emitted, in order to convert the zinc and iron nitrates into sulphates. When cold, it is taken up in water acidified with sulphuric acid, a few drops of hydrogen peroxide added, the liquid heated to convert the basic sulphates

[1] For the electrolytic determination of tin, *see* Ordinary Bronzes.

[2] If the alloy contains bismuth, arsenic and manganese, the determination of the lead cannot be effected simultaneously with that of the copper, since these metals may be deposited on the anode. In this case the lead must be determined by the method indicated for the analysis of delta metal (*see* later: Complex Brasses).

into neutral sulphates and the clear, hot solution treated with ammonia in slight excess. After a short rest on the water-bath, the precipitated ferric hydroxide is filtered off, washed, dried, ignited and weighed [1]: $Fe_2O_3 \times 0{\cdot}6994 = Fe$.

The filtrate now contains only the zinc, which may be estimated with stationary or rotating electrodes in the manner described below. In any case, however, if the brass contains more than 20% of zinc (shown by the weight of copper obtained), it is advisable to make up the volume of the solution to 300 c.c. and to determine the zinc on 150 c.c.[2]

(a) *Determination with stationary electrodes.* The ammoniacal solution is acidified with lactic acid, then rendered faintly alkaline with sodium hydroxide, treated with 3 grams of ammonium oxalate and 5 grams of sodium sulphate, heated gently to dissolve the salts and made up to about 250 c.c. 5 c.c. of lactic acid are then added and the still tepid liquid electrolysed: *coppered* Winkler cathode [3]; Winkler spiral anode; $ND_{100}$ = 0·5–0·6 amp.; voltage = 3–4; duration, 3–4 hours. After about 2 hours, the current intensity is raised to 1 amp. and 2 c.c. of lactic acid are added, the electrolysis being continued until the deposition of the zinc is complete.

To ascertain if all the zinc is deposited, a few drops of the electrolyte are removed and treated with a drop of potassium ferrocyanide: no turbidity should be produced, even after some time. Another method consists in connecting to the upper extremity of the stem of the cathode, by means of a binding screw, a stout copper wire previously cleansed by a brief immersion in nitric acid, and bending this wire twice at right angles so that it dips into the electrolyte for a few centimetres without touching the electrodes: if the wire does not show a faint bluish deposit of zinc after 10–15 minutes, the deposition is complete. The electrolytic beaker is then replaced by a small beaker filled with distilled water, the cathode being detached after some time, washed with water, alcohol and ether and dried at 70°.

(b) *Determination with rotating electrodes.* The ammoniacal solution is acidified with sulphuric acid, rendered alkaline with sodium hydroxide and then faintly acid by means of 25% formic acid solution; the liquid is heated to 40–50° and electrolysed: coppered Winkler cathode [3]; rotating spiral anode; rotations, 1000 per minute; temperature, 40–50°; $ND_{100}$

[1] If there is much ferric hydroxide, it is advisable to precipitate twice to get rid of traces of zinc it may retain.

[2] In the analysis of white brasses (90–95% Zn), the zinc should be determined on an aliquot part of the solution containing about 0·2–0·3 gram of zinc.

[3] *Coppering of platinum electrodes.*—In the electrolytic determination of zinc and also in that of tin, it is convenient to use the coppered cathode because, if these metals are deposited directly on the platinum they form alloys with it and, when the deposited metal is dissolved in acid, the electrode exhibits black spots difficult to remove.

The electrode may be coppered under the conditions given for the electrolytic determination of copper, a solution of copper sulphate acid with nitric acid being electrolysed until the cathode is uniformly covered with copper. A more brilliant coating is obtained by electrolysing, at $ND_{100}$ = 1 amp., a copper sulphate solution treated with an excess of ammonium oxalate and acidified with oxalic acid, at 70–80°. The coppered cathode obtained by either of these methods is washed with water, alcohol and ether, dried at 70° and tared.

= 1–1·5 amp.; voltage = 4–5; duration, 30–40 minutes. During the whole course of the electrolysis, the liquid should be kept faintly acid.

**4. Determination of the Nickel.**—In presence of nickel, the nickel and zinc are determined under the conditions indicated for the electrolytic analysis of argentan.

**5. Determination of the Phosphorus.**—*See* Analysis of Phosphor Bronzes.

**6. Determination of the Arsenic, Sulphur and Bismuth.**—The methods given for the analysis of copper (*q.v.*) are followed.

## *B.* Gravimetric Methods

In a small covered beaker, 0·5 gram of the sample is dissolved in 10–15 c.c. of nitric acid (D 1·2) at a gentle heat.

**1. Determination of the Tin.**—When the action is complete, the solution is diluted with 15–20 c.c. of water and, if it appears turbid owing to the presence of metastannic acid, evaporated to dryness. The residue is heated for some time with a few drops of nitric acid and a little water and the metastannic acid filtered off, washed with hot water acidified with nitric acid, ignited and weighed: $SnO_2 \times 0{\cdot}7881 = Sn$.

**2. Determination of the Lead.**—The liquid freed from the metastannic acid, or the original solution if the alloy does not contain tin, is treated with 3–4 c.c. of concentrated sulphuric acid, evaporated to dryness and heated on a sand-bath until white fumes of sulphuric acid appear. When cool, the residue is taken up in 50 c.c. of water, gently heated and stirred to dissolve the basic copper and zinc sulphates, allowed to cool and mixed with 15 c.c. of 95% alcohol. After standing for 1–2 hours, the lead sulphate separated is collected on a Gooch crucible, washed first with a mixture of 60 c.c. of water, 10 c.c. of alcohol and 0·5 c.c. of sulphuric acid and then with alcohol until the filtrate is neutral; the crucible is then dried in an air-oven in a roomy porcelain crucible: $PbSO_4 \times 0{\cdot}6831 = Pb$.

**3. Determination of the Copper.**—The filtrate from the lead sulphate is evaporated until the alcohol is completely expelled, the residue being heated to boiling with 100 c.c. of water and the copper precipitated with hydrogen sulphide. The liquid is decanted on to a filter and the precipitate washed first with saturated hydrogen sulphide solution containing about 20 c.c. of 2N-sulphuric acid in 100 c.c. and afterwards with saturated hydrogen sulphide solution alone; the precipitate is dried and the copper determined as cuprous sulphide: $Cu_2S \times 0{\cdot}7986 = Cu$.

**4. Determination of the Iron.**—The filtrate is freed from hydrogen sulphide, concentrated to a small volume, treated with a few drops of hydrogen peroxide to oxidise the iron, boiled and rendered alkaline with dilute ammonia. After a short rest on the water-bath, the precipitated ferric hydroxide is filtered, washed, ignited and weighed: $Fe_2O_3 \times 0{\cdot}6994 = Fe$. If the amount of ferric hydroxide is considerable, the precipitation should be repeated to get rid of traces of zinc.

**5. Determination of the Zinc.**—The liquid free from iron is neutralised

exactly, acidified with 8–10 drops of 2N-hydrochloric acid, heated to 50°, treated with about 2% (with reference to the volume of the liquid) of ammonium chloride, and saturated with hydrogen sulphide at 50°. When the zinc is completely precipitated, the zinc sulphide is allowed to settle at a moderate temperature, and is then filtered off, washed with aqueous hydrogen sulphide containing 2 grams of ammonium chloride per 100 c.c. and weighed as zinc sulphide, after being heated in a current of hydrogen in presence of sulphur: $ZnS \times 0{\cdot}6709 = Zn$.

**6. Determination of the Nickel.**—The filtrate from the zinc precipitate is boiled to expel hydrogen sulphide, concentrated, rendered faintly alkaline with ammonia, and the nickel precipitated with alcoholic dimethylglyoxime solution (*see* Analysis of Nickel Steel and of Argentan).

**7. Determination of the Arsenic, Sulphur and Bismuth.**—The methods given for the analysis of copper (*q.v.*) are followed.

**8. Determination of the Phosphorus.**—*See* Analysis of Phosphor Bronze.

***

The ordinary brasses, besides copper and zinc, often contain small quantities of lead and iron (sometimes up to 1%), in some cases tin (0·5–1%) and nickel (0·1–0·3%) and, in general, the impurities present in the copper and zinc used in their preparation.

A good brass should exhibit a fracture of uniform colour and fine and homogeneous grain. It should not contain more than 0·01% of antimony, as otherwise it is brittle and unfit for hammering; it should not contain more than 0·01% of bismuth or 0·1% of arsenic.

The mean percentage compositions of some of the commoner commercial brasses are as follows:

TABLE XXII

**Composition of Brasses**

| Variety. | Cu | Zn |
|---|---|---|
| Pinchbeck, tombac, Mannheim gold (for cheap jewellery) | 85–95 | 5–15 |
| Brass for sheets and plates | 60–72 | 28–40 |
| Brass for tubes | 65–70 | 30–35 |
| Brass for casting | 66–67 | 33–34 |
| Brass for wire | 60–67 | 33–40 |
| White brasses (Fontainmoreau bronzes) | 1–10 | 90–99[1] |
| Brasses for welding | 34–90 | 10–66[2] |

## SPECIAL BRASSES

By this name are indicated those alloys of copper and zinc which contain small quantities of one or more other elements (especially lead, tin, iron, manganese, aluminium) introduced for the purpose of imparting special properties. The most important are as follows.

[1] Often contains 1–2% of lead.
[2] Sometimes contains also small quantities of tin.

## Lead Brasses.

Lead brasses are very soft and therefore suitable for castings to be worked at the lathe. Their analysis comprises, besides determinations of copper and zinc, also that of lead and of the impurities usually occurring in ordinary brass (iron, tin, nickel, sulphur, phosphorus, arsenic, bismuth, etc.). The analytical methods are exactly those used for ordinary brass (*q.v.*).

***

Lead brasses usually contain 1–3% of lead and such impurities as are found in common brass.

## Tin Brasses

Tin brasses are used especially for making tubes, plates, valves, etc., for naval construction. They are analysed by the same methods as ordinary brass (*q.v.*).

***

Tin brasses contain on the average 60–62% Cu, 37·5–39% Zn and 1–1·5% Sn. In this category fall *Naval* brass, *Iton brass* and *Laveyssière bronze*.

## Manganese Brasses

Manganese is introduced in small quantities into brass to increase the strength, elasticity and hardness. The constituents of these brasses are determined as with the complex brasses (*see* later).

***

The two types in most common use have the compositions : (1) 59–60% Cu, 40–41% Zn, traces of Mn, and (2) 58–59% Cu, 39–40% Zn, 1·8–2·2% Mn. They are used in marine construction, especially for making propellers.

The following table gives the compositions prescribed for manganese brasses by the American Society for the Testing of Materials and by the Technical Bureau for Steam Plant of the United States Navy (*Industria*, 1914) :

TABLE XXIII

**Compositions of Manganese Brasses**

| | Cu | Zn | Sn (max.) | Fe (max.) | Al (max.) | Mn (max.) | Pb (max.) |
|---|---|---|---|---|---|---|---|
| American Society for the Testing of Materials . . | 55–60 | 39–45 | 2 | 2 | 0·5 | 0·5 | — |
| Technical Bureau for Steam Plant of U.S. Navy . | 57·60 | 37–40 | 0·75 | 1 | 0·50 | 0·30 | — |
| | 56·68 | 40·42 | 1 | 1 | 0·50 | 0·30 | 0·20 |

## Iron Brasses

The addition of small quantities of iron imparts to brass properties analogous to those of manganese brasses, and iron brasses have the same applications as the latter. The analytical procedure is that indicated for common brass (*q.v.*).

***

The iron brasses in more common use have the following mean compositions :

*Sterro metal* : 55–60% Cu, 38–42% Zn, 1·5–2% Fe, 0–0·8% Sn.
*Aich's metal* : 58–60% Cu, 36–41% Zn, 0·7–1·8% Fe, 0–1% Sn.

## Aluminium Brasses

Aluminium brasses have properties similar to those of manganese and iron brasses and find the same uses in naval construction. They are analysed by the methods for complex brasses (*q.v.*).

***

The aluminium brasses in more common use have the following mean percentage compositions (Guillet) :

(1) Copper, 68–70 ; zinc, 31–27 ; aluminium, 3–1.
(2) ,, 64–66 ; ,, 33–30 ; ,, 4–1.
(3) ,, 58–61 ; ,, 40·5–37·5 ; ,, 1·5–3.

## COMPLEX BRASSES

Complex brasses have properties very similar to those of manganese brasses and are largely used, particularly for making propellers, anchors, keels, torpedo tubes, etc.

These brasses may contain at the same time : iron and manganese ; iron and aluminium ; iron, manganese, aluminium and, sometimes, tin. Their analysis includes determinations of the components proper (Cu, Zn, Mn, Fe, Al, Sn) and of any extraneous elements present as impurities (Pb, P, S, Bi, etc.), and may be carried out electrolytically or by a combined gravimetric and volumetric method.

### *A.* Electrolytic Method[1]

In a small covered beaker, 1 gram of the sample is dissolved in 10–12 c.c. of nitric acid (D 1·2) at a gentle heat.

**1. Determination of the Tin.**—The solution is diluted with 15–20 c.c. of water and, if turbid owing to the presence of metastannic acid, evaporated to dryness, the residue being taken up with a few drops of nitric acid and a little water. The liquid is heated for some time and the metastannic acid filtered off, washed with hot water acidified with nitric acid, ignited and weighed : $SnO_2 \times 0{\cdot}7881 = Sn$.

[1] **Belasio and Marchionneschi** : *Annali di Chimica applicata*, 1914, 1, p. 127.

**2. Determination of the Lead.**—The liquid freed from metastannic acid, or the original solution if the alloy does not contain tin, is evaporated on a sand-bath with 5 c.c. of dilute sulphuric acid (1 vol. acid to 1 vol. water) until copious white fumes are emitted. When cold, the residue is heated gently and stirred with 50 c.c. of water to dissolve the basic sulphates of copper, zinc, etc., and the solution, after cooling, mixed with 15 c.c. of 95% alcohol. After standing for 1–2 hours, the lead sulphate which separates is collected in a Gooch crucible and is washed first with a mixture of 60 c.c. water, 10 c.c. of alcohol and 0·5 c.c. of sulphuric acid and then with alcohol until the reaction is neutral; it is then dried, heated and weighed: $PbSO_4 \times 0{\cdot}6831 = Pb$.

**3. Determination of the Copper.**—The filtrate is evaporated almost to dryness to eliminate the alcohol, the residue being diluted with water to 150 c.c. and electrolysed at the ordinary temperature. Cathode, Winkler electrode; anode, spiral; $ND_{100} = 0{\cdot}1–0{\cdot}2$ amp.; voltage, 1·7–2; duration, 15–16 hours.

During the whole course of the electrolysis, the voltage at the terminals should never exceed 2, so that it is advisable to use a single accumulator or a battery of accumulators joined in parallel. At the completion of the deposition, the electrolytic beaker is lowered slowly and the electrodes washed as they emerge. The washing of the cathode is completed with water, alcohol and ether, and the weight determined after drying at 70°.

**4. Separation of the Iron and Manganese.**—The spiral anode, which is covered with a black coating of manganese dioxide, is immersed in the liquid from which the copper has been separated, this being heated with addition of 3–4 drops of hydrogen peroxide until the manganese dioxide is completely dissolved. The spiral is withdrawn and washed, and the solution concentrated to 30–40 c.c. and poured, little by little and with shaking, into a solution of 10 grams of pure sodium hydroxide in 30–40 c.c. of water contained in a platinum or porcelain dish. The iron and the manganese are precipitated as oxides, while the zinc and aluminium pass into solution as sodium zincate and aluminate. The liquid is heated to boiling, diluted with boiling water and filtered, the filtrate being collected in a half-litre beaker containing about 100 c.c. of 20% sulphuric acid and the filter washed with hot water. The oxides separated are dissolved in a little dilute sulphuric acid containing a few drops of hydrogen peroxide and the solution again poured into sodium hydroxide solution of the concentration mentioned above, the latter being heated to boiling, diluted and filtered and the filtrate collected in the same half-litre beaker as the other.

(*a*) DETERMINATION OF THE IRON. The ferric and manganese hydroxides are redissolved in the least possible quantity of 10% sulphuric acid, a few drops of hydrogen peroxide being added and the solution heated. The greater part of the free acid is neutralised with ammonia and the solution poured into a boiling solution of 6–7 grams of ammonium oxalate in a little water; after addition of 5–6 c.c. of 2% hydrazine sulphate solution and dilution to about 200 c.c., the liquid is electrolysed to determine the iron (*see* Ferro-manganese, Electrolytic Analysis).

(*b*) DETERMINATION OF THE MANGANESE. The liquid from which the

iron has been separated is concentrated, with the anode immersed, to 60–70 c.c. and the manganese determined as indicated in the electrolytic analysis of ferro-manganese.

**5. Determination of the Zinc.**—If not already acid, the solution containing the zinc and aluminium is acidified with dilute sulphuric acid, evaporated if necessary to reduce the volume to 200–250 c.c., rendered alkaline with sodium hydroxide, acidified slightly with formic acid and electrolysed with rotating electrodes to determine the zinc (*see* p. 225).

**6. Determination of the Aluminium.**—The liquid from which the zinc has been removed, together with wash water, is treated with ammonium chloride and ammonia until the reaction is alkaline, boiled for some time and the aluminium hydroxide filtered off, washed, dried, ignited and weighed: $Al_2O_3 \times 0{\cdot}5303 = Al$.

**7. Determination of the Phosphorus, Sulphur, Bismuth, Arsenic, etc.**—*See* Ordinary Brass.

## *B.* Combined Gravimetric and Volumetric Method

2 grams of the sample are dissolved in 20 c.c. of nitric acid (D 1·2) at a gentle heat.

**1. Determination of the Tin, Lead and Copper.**—The liquid is diluted with 15–20 c.c. of water, and the tin, lead and copper determined gravimetrically as in ordinary brass (*q.v.*).

**2. Determination of the Iron, Manganese, Zinc and Aluminium.**—The liquid from which the copper has been separated as sulphide is evaporated to reduce its volume to about 200 c.c. and to expel the hydrogen sulphide, the iron being oxidised by addition of a few drops of hydrogen peroxide and the cooled liquid made up to 300 c.c.

(*a*) VOLUMETRIC DETERMINATION OF THE IRON. The iron in 50 c.c. of this solution is reduced with zinc amalgam and titrated with permanganate in the usual way.

(*b*) VOLUMETRIC DETERMINATION OF THE MANGANESE. Two other portions, each of 50 c.c., are used for the determination of the manganese by Volhard's method (*see* Ferro-manganese), one for the preliminary test and the other for the actual determination.

(*c*) DETERMINATION OF THE ZINC. A further quantity of 50 c.c. is rendered alkaline with ammonia and then neutralised with formic acid; for each 100 c.c. of this solution 4 c.c. of 50% formic acid are added and the zinc precipitated by hydrogen sulphide. The liquid is left overnight to complete the precipitation and is then filtered through a filter-paper of compact texture and washed with a dilute solution of ammonium formate saturated with hydrogen sulphide.[1]

When completely washed, the precipitate is dried and introduced into a Rose crucible, the filter being burned in a platinum spiral and dropped into the crucible. The precipitate is then mixed by means of a platinum

[1] The ammonium formate solution is prepared by neutralising a dilute solution of formic acid (1–2%) with ammonia and slightly acidifying with formic acid.

wire with about one-third of its weight of pure sulphur and heated in a current of hydrogen to constant weight: $ZnS \times 0{\cdot}6709 = Zn$.

(*d*) DETERMINATION OF THE ALUMINIUM. The liquid from which the zinc has been removed is concentrated in a porcelain dish to small volume, the iron being then oxidised with hydrogen peroxide and the solution rendered alkaline with pure potassium hydroxide solution, boiled, diluted with boiling water and filtered. The filter is washed with hot water and the filtrate acidified with nitric acid, rendered alkaline with ammonia and heated to boiling for a short time. The precipitated aluminium hydroxide is filtered off, washed, dried to some extent, ignited in a platinum crucible and weighed: $Al_2O_3 \times 0{\cdot}5303 = Al$.

**3. Determination of the Phosphorus, Sulphur, Arsenic, Bismuth, etc.**—*See* Ordinary Brasses.

***

Of these complex brasses the one most largely used is the so-called "Delta metal," of the following mean composition: 54–62% Cu, 38–40% Zn, 0·5–3% Mn, 0·4–1·2% Fe, 0·02–2·5% Al, 0–0·5% Pb and 0–3% Sn.

## ORDINARY BRONZES

Analysis of ordinary bronzes includes, besides determinations of the constituent metals (copper, tin and sometimes zinc), also those of the extraneous metals often present in small quantities (lead, iron, antimony, nickel, manganese, phosphorus, arsenic, sulphur, etc.). Electrolytic or gravimetric methods may be used.

### *A.* Electrolytic Method

In a covered beaker, 1–3 grams of the alloy, as filings or turnings, are treated in the cold with 15–20 c.c. of nitric acid (D = 1·3), the liquid being heated gently when the action slackens and finally evaporated almost to dryness.

**1. Determination of the Tin.**—The residue is taken up with a few drops of nitric acid, 50 c.c. of water being mixed in and after about an hour on the water-bath, the liquid filtered through a compact filter-paper and the residue on the filter washed with hot water acidified with nitric acid (1 of acid to 100 of water). The filtrate is utilised as described in 3 (below). The metastannic acid separated may be dried, ignited and weighed, but it may contain various impurities (especially copper and phosphorus), and when an exact analysis is required the following procedure is advisable.[1]

[1] The method of fusion with sulphur and sodium carbonate indicated for the gravimetric analysis of bronzes (*see* p. 234) may also be used and, when the antimony has been removed by means of hydrogen sulphide, the electrolytic method followed.

Further, in absence of phosphorus and antimony the following simpler procedure may be employed. The impure stannic oxide is separated and weighed and then disintegrated with sulphur and sodium carbonate, the resulting fused mass being taken up in hot water. The copper sulphide is separated and determined and the corresponding weight of the oxide deducted from the sum, $SnO_2 + CuO$. The remainder represents pure stannic oxide, which gives the tin present in the sample. The copper occluded in the stannic oxide is added to the amount found in the nitric acid solution.

The filter and precipitate are heated with 2–3 c.c. of 10% sodium hydroxide, and 10–15 c.c. of sodium sulphide solution (D 1·225) in a small beaker on a water-bath until the metastannic acid is completely dissolved. After dilution with 10–15 c.c. of water and addition of a little sodium sulphite dissolved in a little water to reduce polysulphides, the liquid is again heated for a short time and filtered by decantation, the filtrate being collected in a ¾-litre conical flask. The residue is again treated with 10–15 c.c. of sodium sulphide solution, heated, reduced with sulphite, diluted, filtered and washed with hot water containing a little sodium sulphide until about 150–200 c.c. of filtrate are collected. The lead, copper, iron, etc., contained in the metastannic acid remain on the filter as sulphides. The filter is dried and then burnt in a small dish, the residue being dissolved in a little nitric acid (D 1·3) and the solution obtained added to the liquid in which the copper, lead, zinc, etc., are to be determined.

As regards the determination of the tin and antimony, hydrochloric acid diluted with an equal volume of water is added gradually and with shaking (under a draught hood) to the solution in sodium sulphide until the latter shows an acid reaction; 25–30 c.c. of concentrated hydrochloric acid are then added and the liquid boiled to dissolve the separated sulphides, adding, if necessary, a few crystals of potassium chlorate.

When cold, the solution—which contains sulphur and is turbid—is rendered alkaline with ammonia and then heated with 5 grams of oxalic acid. When all the tin hydroxide precipitated by the addition of ammonia is redissolved, 7 grams of ammonium oxalate are added, the liquid heated to boiling and hydrogen sulphide passed for about 15 minutes through the boiling liquid. Under these conditions, any antimony present is alone precipitated.

After being allowed to cool somewhat in the current of hydrogen sulphide, the liquid is filtered, the filtrate being collected in a ½-litre beaker and the washing effected with a hot 1% oxalic acid solution saturated with hydrogen sulphide. The antimony sulphide precipitate remaining on the filter is analysed according to 2 (below).

The filtrate is treated with 30 c.c. of conc. hydrochloric acid and 20 grams of ammonium oxalate, boiled for a short time to eliminate hydrogen sulphide, a few drops of hydrogen peroxide added, heated again for a short time, allowed to cool to 40–50°, made up to about 300° and electrolysed, if possible under a hood, to determine the tin: coppered Winkler cathode [1]; spiral anode; $ND_{100} = 1$ amp.; voltage = 3–4; temperature, 40–50°, and duration (with 0·1–0·3 gram Sn) 4–5 hours.

When the deposition of the tin is complete, the electrolytic beaker is replaced, without interrupting the current, by another full of water; after a time the cathode is detached, washed with an abundant supply of water and then with alcohol and ether, and dried at 70°.

[1] To prevent attack of the copper coating by the acid solution while the arrangements for the electrolysis are being made, the electrodes should be fixed on supports at the required height and connected with the source of current, the beaker being then raised to immerse them. In this way the current begins to flow immediately the electrodes dip into the liquid and so prevents attack of the copper.

**2. Determination of the Antimony.**—The filter-paper with the antimony sulphide is heated in a beaker with 4 c.c. of 50% sodium hydroxide solution and 20–30 c.c. of sodium sulphide (D = 1·225) until the antimony sulphide is completely dissolved. After some time the liquid is filtered directly into the Classen dish, the vessel and filter being washed with 50–60 c.c. of sodium sulphide. The filtrate is treated with 5–6 grams of potassium cyanide to decolorise the sodium sulphide and to prevent formation of polysulphides during the electrolysis, which is carried out at the ordinary temperature. Cathode, Classen capsule; anode, disc or spiral; $ND_{100}$ = 0·15–0·18 amp.; voltage = 1–1·2; duration (0·1–0·15 gram Sb) = 15–18 hours.

When the antimony is all deposited, the anode is withdrawn, the capsule rapidly emptied, washed with water, alcohol and ether, and dried at 70°.

The antimony is afterwards removed from the dish by treatment with nitric acid (D 1·2) containing a little tartaric acid in solution.

**3. Determination of the Copper, Lead, Iron and Zinc.**—The liquid from which the metastannic acid was separated (*see* 1) is acidified with 15–20 c.c. of nitric acid (D 1·2), mixed with the nitric acid solution of the oxides extracted from the metastannic acid and the whole treated as in the analysis of ordinary brass (*q.v.*).

**4. Determination of the Nickel.**—*See* Nickel Bronzes.

**5. Determination of the Manganese.**—*See* Manganese Bronzes.

**6. Determination of the Silver.**—5–10 grams of the sample are treated with nitric acid and freed from metastannic acid in the ordinary way. In the filtrate the silver is precipitated with hydrochloric acid by the procedure followed for the determination of silver in copper.[1]

**7. Determination of the Phosphorus.**—*See* Phosphor Bronzes.

**8. Determination of the Arsenic.**—*See* Copper.

**9. Determination of the Sulphur.**—2 grams of the sample are treated with nitric acid and the stannic acid separated as usual. From the filtrate the copper is eliminated by electrolysis in nitric acid solution, the residual liquid being evaporated to dryness and the sulphur then determined as in copper (*q.v.*).

## *B.* Gravimetric Method

**1. Determination of the Tin.**—In a covered beaker, 1–2 grams of the alloy as filings are treated with 15–20 c.c. of nitric acid (D 1·3), the metastannic acid being separated, washed, ignited in a porcelain crucible and weighed: $SnO_2 \times 0{\cdot}7881 = Sn$. The filtrate is treated as in 3.

The stannic oxide thus weighed is always impure and, where an exact determination is necessary, it is powdered in an agate mortar, mixed with 6 parts of a mixture of ignited sodium carbonate and sulphur in equal proportions, and heated at a gentle heat with the crucible covered until all the sulphur is expelled.

[1] Since silver is deposited with the copper on the cathode, the data relating to copper must be corrected by the amount found.

When cold, the mass is taken up in hot water and the brown solution heated with sodium sulphite until it becomes pale yellow.[1] The liquid is then filtered and, the precipitate washed with water containing a little sodium sulphide and then with hydrogen sulphide solution; the filter is burnt in a small dish and the residue dissolved in a little nitric acid and the solution added to the filtrate from the metastannic acid containing the bulk of the copper, lead, zinc, etc., dealt with as in 3.

The solution contains all the tin and antimony present as sulpho-salts. This liquid is treated in a ¾-litre conical flask with 6 grams of caustic potash, 3 grams of tartaric acid and, slowly and, if necessary, with cooling, with sufficient 30% hydrogen peroxide to give complete decoloration, that is, to convert the sulphide completely into sulphate. The liquid is boiled for some time to expel excess of hydrogen peroxide, allowed to cool, neutralised carefully with oxalic acid, treated with an excess of 3–5 grams of oxalic acid, diluted to 250–300 c.c., heated to boiling, and a moderate current of hydrogen sulphide passed through the boiling liquid for about an hour. The liquid is then allowed to cool somewhat and any precipitated antimony sulphide collected in a tared Gooch crucible, and washed first with 1% oxalic acid solution saturated with hydrogen sulphide and afterwards with very dilute hot acetic acid saturated with hydrogen sulphide.

To determine the tin, the filtrate is rendered slightly alkaline with ammonia, acidified with acetic acid, and the tin precipitated with hydrogen sulphide. After the precipitation, the liquid is left at rest for about half an hour on the water-bath to facilitate the separation of the precipitate, and finally filtered, being washed with hydrogen sulphide solution containing a little ammonium sulphate in solution. The tin sulphide thus obtained is dried at 120°, converted by ignition into oxide and weighed.

**2. Determination of the Antimony.**—The antimony sulphide in the Gooch crucible is converted by any of the known methods[2] into the trisulphide and weighed directly: $Sb_2S_3 \times 0{\cdot}7142 = Sb$.

**3. Determination of the Lead, Copper, Iron, Zinc, etc.**—The filtrate obtained after the action of nitric acid on the alloy, together with the nitric acid solution of the metals extracted from the metastannic acid, is treated with 2–3 c.c. of conc. sulphuric acid, the further procedure being as given for the analysis of ordinary brasses (*q.v.*).

**4. Determination of the Manganese, Silver, Phosphorus, Arsenic and Sulphur.**—*See* preceding method.

***

The compositions of bronzes vary widely with the requirements as regards hardness, elasticity, colour, sonority, etc.

Bronzes for machine gearing and the old, highly elastic, tenacious and resistant bronzes for cannon contained on the average 90% Cu and 10% Sn; those for cocks, cast machine parts, etc., 87% Cu, 13% Sn, and often small amounts of zinc; those for bushes and collars, 82–84% Cu and 16–18% Sn. Bronzes for

[1] If the residue insoluble in water has a sandy aspect, the disaggegration is incomplete. In such case the filter is dried and burnt and the residue again fused with sulphur and sodium carbonate.

[2] See Treadwell: *Analytical Chemistry*, Vol. II.

bells, very hard and sonorous but brittle, contain usually 75–80% Cu, 20–25% Sn, and sometimes small quantities of zinc, lead, silver, etc. Silver-coloured bronzes for small, highly sonorous bells contain 40–42% Cu and 58–60% Sn. Statuary bronze contains also considerable proportions of zinc (78–90% Cu, 2–4% Sn, 10–18% Zn).

As a rule commercial bronzes, besides copper and tin, contain small quantities of other elements (especially zinc, iron, manganese, nickel, lead, antimony, phosphorus, arsenic, sulphur, etc.), which, even in small proportions, may profoundly modify the properties of the alloy (*see* Special Bronzes) ; so much is this the case that it is not always easy to decide if these elements are impurities of the raw materials used or if they have been added to obtain certain specific properties.

Zinc in small quantities (0·5–2%) renders bronze more easy to cast and increases its strength and elasticity ; if, however, the proportion is slightly greater than 2%, the bronze loses its hardness and strength and assumes properties approximating to those of the brasses.

The presence of lead is especially harmful in bronzes for machines and tools, even if it is only slightly greater than 0·5%, since it diminishes the homogeneity of the alloy. In proportions not exceeding 1·5%, iron exerts an action analogous to that of zinc and increases considerably the hardness of the bronze. Arsenic, antimony, bismuth and sulphur are highly injurious, and even in the proportion of 0·1% render the bronze brittle. Nickel, manganese and phosphorus improve the quality of the alloy and are often added (*see* Nickel-bronze, Manganese-bronze, Phosphor-bronze, etc.).

## SPECIAL BRONZES

These are copper-tin alloys containing another element added with a definite object. Those in more common use are : phosphor-, silicon-, manganese-, lead-, nickel-, lead-nickel- and aluminium-bronzes.

### Phosphor-bronzes

Phosphor-bronzes are so called because during their preparation a small quantity of phosphorus is added as phosphor-copper or phosphor-tin with a view to reduce the metallic oxides contained in the metal and, therefore, to impart greater hardness, strength, elasticity, etc. The attempt is usually made to add the quantity of phosphorus just necessary for the deoxidation (there may, therefore, be phosphor-bronzes free from phosphorus), or at most only a slight excess, so that only a very small amount passes into the alloy. The analysis includes determinations of the usual constituents and impurities and also that of phosphorus.

**1. Determination of the Phosphorus.**—(*a*) IN ABSENCE OF ARSENIC. 2 grams of the sample are dissolved in aqua regia or in hydrochloric acid and potassium chlorate, the solution being repeatedly evaporated to dryness with hydrochloric acid, the residue then dissolved in dilute hydrochloric acid and water and the phosphoric acid precipitated with ammonium molybdate as in the determination of phosphorus in iron (*see* p. 173).

(*b*) IN PRESENCE OF ARSENIC. After the repeated evaporation with hydrochloric acid, the residue is taken up twice in hydrobromic acid and evaporated to dryness each time. The residue is then taken up in conc. hydrochloric acid, evaporated to dryness, the residue dissolved in dilute

hydrochloric acid and the phosphoric acid precipitated in the usual way (*see* Determination of Phosphorus in Iron in presence of Arsenic).

**2. Determination of Tin, Copper, Zinc, etc.**—*See* Ordinary Bronzes.[1]

***

In some bronzes for bushes, pistons, etc., subject to attrition, quantities of phosphorus varying from 0·25 to 2·5% are sometimes present with a view to obtaining quite special effects. In ordinary phosphor-bronzes smaller quantities are found (less than 0·25%).

## Silicon-bronzes

These are used especially for telegraph and telephone wires, as they have high electrical conductivity and resistance to tension. Their analysis includes:

**1. Determination of Silicon.**—2–10 grams of the sample, according to the supposed silicon content, are treated with aqua regia (3 parts of hydrochloric acid and 1 part of nitric acid), the solution being evaporated to dryness, the residue taken up twice with about 15 c.c. of concentrated hydrochloric acid and evaporated, and the residue heated in an oven at 135° to render the silica completely insoluble. The residue is treated with hydrochloric acid, the subsequent procedure being as in the determination of silicon in iron. In the present case also the purity of the silica must be investigated by treatment with sulphuric and hydrofluoric acids.

**2. Determination of the Tin, Iron, Zinc, Nickel, Phosphorus, Sulphur, etc.**—As with ordinary bronzes[2] (*q.v.*).

***

Silicon-bronzes, besides a little tin and often a little zinc, contain very small quantities of silicon (0·05–1%) introduced in the form of silicon-copper as a deoxidiser. According to Hampe the best bronzes for telegraph and telephone wires have the following percentage compositions:

TABLE XXIV

**Compositions of Silicon-bronzes**

| | Cu | Sn | Si | Fe | Zn |
|---|---|---|---|---|---|
| For telephone wires . | 97·12 | 1·14 | 0·05 | trace | 1·12 |
| For telegraph wires . | 99·94 | 0·03 | 0·03 | trace | — |

## Lead-bronzes

Lead-bronzes, also called American bronzes owing to their widespread use in America, besides copper and tin contain considerable quantities of lead and sometimes phosphorus, and are used for bearings and parts of machines subject to friction, the lead increasing largely the plasticity of the alloy. Their analysis includes:

**1. Determination of the Tin, Lead, Copper, Iron, Zinc, etc.**—

[1] The presence of phosphorus in the metastannic acid separating to be borne in mind.

[2] The presence of silica in the metastannic acid separating to be borne in mind.

1 gram of the alloy is dissolved in 15–20 c.c. of nitric acid (D 1·3), the solution evaporated to dryness, the residue taken up with a few drops of nitric acid and hot water, and the separate determinations carried out as with ordinary bronzes (*q.v.*).

**2. Determination of the Phosphorus.**—1 gram of the sample, as filings, is dissolved in aqua regia, evaporated to dryness, repeatedly taken up with hydrochloric acid and evaporated to dryness, and the residue dissolved in dilute hydrochloric acid and hot water (400–500 c.c.) and the hot solution treated with hydrogen sulphide. The precipitate is washed on a Gooch crucible with hot water saturated with hydrogen sulphide and acidified with hydrochloric acid and the filtrate evaporated to dryness with nitric acid.

The residue is dissolved in a little nitric acid and the phosphoric acid precipitated with ammonium molybdate as in the determination of phosphorus in iron.

***

The following table gives the compositions of various types of commercial lead-bronzes (Guillet, Muspratt, Ledebur) :

TABLE XXV

**Composition of Lead-bronzes**

| | Cu | Sn | Pb | Zn | P | Fe | Sb | Ni | As |
|---|---|---|---|---|---|---|---|---|---|
| 1 . . . | 84·70 | 10·05 | 4·00 | 0·46 | 0·11 | — | 0·14 | — | — |
| 2 . . . | 84·00 | 3·00 | 4·56 | 8·50 | — | — | — | — | — |
| 3 . . . | 83·85 | 8·32 | 7·36 | 0·13 | 0·31 | trace | — | — | 0·04 |
| 4[1] . . . | 79·70 | 10·00 | 9·50 | — | 0·80 | — | — | — | — |
| 5 . . . | 73·50 | 9·50 | 9·50 | 9·50 | — | 0·50 | — | — | — |
| 6 . . . | 78·01 | 10·36 | 10·45 | — | 0·57 | 0·09 | — | 0·26 | — |

## Manganese-bronzes

Manganese-bronzes, which should not be confused with manganese-brasses—often improperly given this name—or manganese-copper alloys, are composed essentially of copper and tin with small proportions of manganese (1–3%). Their analysis comprises :

**1. Determination of the Tin.**—As in ordinary bronzes.

**2. Determination of the Lead, Copper, Iron, Manganese and Zinc.**—The liquid from which the metastannic acid has been separated, together with the solution of the metals occluded in the metastannic acid, is evaporated with sulphuric acid and the separate determinations carried out as with complex brasses.

**3. Determination of the Phosphorus, Arsenic and Sulphur.**—*See* Ordinary Bronzes.

[1] Type adopted by the Italian State Railways.

The compositions of the commoner commercial types of manganese-bronzes are as follows (Guillet) :

TABLE XXVI

**Composition of Manganese-bronzes**

| | Cu | Sn | Zn | Mn | P |
|---|---|---|---|---|---|
| 1 . . . | 92 | 8 | — | 1 | — |
| 2 . . . | 84 | 14 | — | 2 | — |
| 3 . . . | 82 | 15 | — | 3 | — |
| 4 . . . | 92 | 8 | 3 | 0·5 | trace |

## Nickel-bronzes

The addition of small proportions of nickel to bronzes increases the hardness and lustre and imparts a pleasing, golden colour.

Their analysis includes :

**1. Determination of the Tin.**—2 grams of the sample are treated in a covered, tall, narrow beaker with 20 c.c. of nitric acid (D 1·2), the solution being evaporated to dryness, taken up with a few drops of nitric acid and hot water and heated for a short time on the water-bath. The metastannic acid is collected on a close filter-paper and, being in small quantity, may be weighed directly after washing with hot water acidified with nitric acid, drying and calcining.

**2. Determination of the Lead, Copper, Iron, Nickel and Zinc.**—These elements are determined in the liquid freed from metastannic acid by the methods given for the analysis of argentan (*see* later).

**3. Determination of the Phosphorus, Arsenic and Sulphur.**—*See* Ordinary Bronzes.

***

Nickel-bronzes have the following mean composition : 88–89% Cu, 2–3% Sn, 6–7% Zn, 2–3% Ni, and 0·1–0·3% Pb.

## Lead-nickel-bronzes

These are very soft and are also called plastic bronzes and serve mostly as antifriction metals. Their analysis comprises :

**1. Determination of the Tin.**—2 grams of the alloy are dissolved in a covered, tall, narrow beaker with 20 c.c. of nitric acid (D 1·3), the solution evaporated to dryness, and the analysis continued as with ordinary bronzes (*q.v.*).

**2. Determination of the Lead.**—The solution freed from metastannic acid and the solution of the oxides of copper and lead retained by the metastannic acid are evaporated together to a small volume and then heated

on a sand-bath with 3–4 c.c. of conc. sulphuric acid until white fumes of sulphuric acid appear. The lead is determined as sulphate in the way given for the gravimetric analysis of ordinary brasses.

**3. Determination of the Copper, Iron, Nickel and Zinc.**—(*a*) ELECTROLYTICALLY. The liquid freed from lead is evaporated until the alcohol is expelled and the residual liquid mixed with 20 c.c. of nitric acid and electrolysed as in the case of argentan.

(*b*) GRAVIMETRICALLY. The liquid freed from lead is evaporated to eliminate the alcohol, mixed with 200–250 c.c. of water, heated to boiling and the copper precipitated with hydrogen sulphide, the subsequent procedure being that described for the gravimetric analysis of argentan.

**4. Determination of the Phosphorus, Arsenic and Sulphur.**—*See* Ordinary Bronzes.

***

Lead-nickel-bronzes have the following mean composition: 64% Cu, 30% Pb, 5% Sn, and 1% Ni.

## Aluminium-bronzes

Aluminium-bronzes have a fine, golden-yellow colour and are used for making vases, ornamental articles, etc. They consist essentially of copper and aluminium (3–10%) and often contain small quantities of silicon and iron. Their analysis includes:

**1. Determination of the Silicon.**—1 gram of the alloy is heated gently with 10 c.c. of nitric acid (D 1·2) and the solution evaporated with 10 c.c. of 50% sulphuric acid until white fumes of sulphuric acid appear. The residual liquid is mixed with 30 c.c. of water, heated for some time and, when cold, filtered through a small filter; the residue of more or less pure silica is washed, dried, calcined in a platinum crucible and weighed. It is then treated with hydrofluoric acid, etc., as in the determination of silicon in iron.

**2. Determination of the Copper.**—The filtrate is treated with 4–5 c.c. of nitric acid, diluted to about 150 c.c. and subjected to electrolysis (*see* Electrolytic Determination of Copper in Ordinary Brasses).

**3. Determination of the Iron and Aluminium.**—After removal of the copper, the liquid is rendered alkaline with ammonia, boiled for some time and the precipitated aluminium and ferric hydroxides filtered off, washed, calcined and weighed. The oxides are then fused with potassium bisulphate, the residue taken up in dilute sulphuric acid and the iron in the solution determined electrolytically or volumetrically. The iron and aluminium are thus obtained separately.

***

The compositions of the more important industrial types of aluminium-bronzes are as follows (Guillet):

TABLE XXVII

**Composition of Aluminium-bronzes**

| | Cu | Al | Si | Fe |
|---|---|---|---|---|
| 1 . . . . . | 92–96 | 4–8 | — | — |
| 2 (for automobiles) . . | 94·9 | 4·7 | 0·41 | 0·10 |
| 3 do. . . | 95·4 | 4·0 | 0·33 | 0·12 |
| 4 do. . . | 97·0 | 2·7 | 0·19 | 0·20 |

# ZINC AND ITS ALLOYS

In this place zinc as such will be treated and methods described for determining its common impurities; technical tests for zinc dust are also given. As regards the numerous alloys in which zinc occurs, those with copper are dealt with under copper and its alloys and those with nickel under nickel and its alloys.

## ZINC

The extraneous elements commonly found in commercial zinc are lead, iron and cadmium. Small quantities of arsenic, antimony and sulphur are also often found and in remelted zinc also tin, but only rarely are traces of carbon, silicon, phosphorus, copper, nickel, cobalt, etc., found.

The essential determinations to be made on commercial zinc are those of lead, iron and cadmium. It may sometimes be of interest to estimate the arsenic, antimony and sulphur, but as a rule it is sufficient to test qualitatively for the other elements.

**1. Determination of the Lead, Iron and Cadmium** (according to Mylius and Fromm [1]).—To 100 grams of the sample and 200 c.c. of water, in a flask holding about 2 litres, nitric acid is added gradually until, with gentle heating, the metal is completely attacked.

The solution obtained is then treated with ammonia until the zinc hydroxide at first separating redissolves, and then diluted to about two litres, very dilute ammonium sulphide being next added in small quantities and with stirring until the lead, iron and cadmium are completely precipitated and zinc sulphide begins to appear.[2] The liquid is kept at 80° for a short time to facilitate separation of the precipitate, which consists of lead, cadmium, iron, etc., sulphides mixed with zinc sulphide, and is filtered off when the supernatant solution becomes clear. The precipitate is treated on the filter with hot, dilute hydrochloric acid,[3] which dissolves lead, cadmium

[1] *Zeitschr. analyt. Chem.*, 1897, p. 37.

[2] A small portion of the liquid, filtered and treated with ammonium sulphide, should yield a distinctly white precipitate.

[3] 2N-Hydrochloric acid (20 c.c. of conc. HCl made up to 100 c.c.). It is advisable to place the acid in a wash-bottle and to wash with it also the flask in which the precipitation took place. About 150–200 c.c. to be used in all.

and iron sulphides, these being estimated as under *a*, *b* and *c* (below) ; the copper and silver sulphides, which remain undissolved, may be dissolved in nitric acid and estimated by the ordinary methods.

(*a*) DETERMINATION OF THE LEAD. The hydrochloric acid solution is evaporated in presence of sulphuric acid and heated until white fumes appear, the cold residue being taken up in water and alcohol added ; the subsequent procedure is as in the gravimetric determination of lead in brass (*see* p. 226).

(*b*) DETERMINATION OF THE CADMIUM. The liquid freed from lead sulphate is evaporated until the alcohol is expelled, neutralised exactly with ammonia, treated for every 100 c.c. of liquid with 10 c.c. of 25% hydrochloric acid (D 1·125) and then with hydrogen sulphide. The precipitate is filtered off, washed with saturated hydrogen sulphide solution and dissolved in nitric acid (D 1·2), the solution being evaporated in a tared platinum crucible in presence of a slight excess of sulphuric acid, the excess of the latter being eliminated and the residue heated gently and weighed : $CdSO_4 \times 0{\cdot}5392 = Cd$.

(*c*) DETERMINATION OF THE IRON. The excess of hydrogen sulphide is eliminated from the filtrate from the cadmium sulphide, the iron being oxidised by a few drops of hydrogen peroxide or bromine water, and ammonia added until the reaction is alkaline. After a short rest on a water-bath, the precipitated ferric hydroxide is filtered and washed. To free the precipitate from all traces of zinc, it is redissolved in dilute hydrochloric acid, again precipitated with ammonia, filtered off, washed with slightly ammoniacal water, dried, ignited and weighed : $Fe_2O_3 \times 0{\cdot}6994 = Fe$.

**2. Determination of the Sulphur, Antimony and Arsenic** (according to Gunther [1]).—100 grams of the sample are placed in a large flask furnished with a delivery tube and with a tapped funnel, the stem of which, bent up at the end, reaches almost to the bottom of the vessel. The air is expelled by means of pure hydrogen washed by passing it through silver nitrate solution and the delivery tube connected with two washing bottles, the first containing a solution of cadmium cyanide in potassium cyanide and the second silver nitrate solution, pure dilute sulphuric acid being then gradually introduced by means of the tapped funnel until the metal dissolves completely. When evolution of gas ceases, a moderate current of hydrogen is passed through the apparatus to displace the gaseous products of the reaction. The first washing bottle retains the sulphur as cadmium sulphide, which is filtered off and converted into sulphate (*see* 1) and weighed.

In the second bottle, if hydrogen arsenide and antimonide are present, metallic silver and silver antimonide [2] separate. The precipitate is filtered off, washed and dissolved in nitric and tartaric acids, the silver being then precipitated as chloride, which is filtered off, washed, dried and weighed. In the filtrate, the greater part of the acidity is neutralised with ammonia

[1] *Zeitschr. analyt. Chem.*, 1881, XX, p. 503.

[2] The reaction occurs according to the equations :

$$SbH_3 + 3AgNO_3 + aq. = Ag_3Sb + 3HNO_3 + aq.$$
$$2AsH_3 + 12AgNO_3 + 3H_2O = 12Ag + 12HNO_3 + As_2O_3.$$

and the antimony precipitated with hydrogen sulphide and weighed as trisulphide or oxide. The silver corresponding with the amount of antimony found ($Ag_3Sb$) is deducted from the total silver found, and the arsenic corresponding with the remainder calculated: 2As = 12Ag.

***

Refined zinc of good quality should not contain more than 1·5% of extraneous elements (Pb, Fe, Cd, Cu, etc.) and not more than 0·1% of As, Sb and S together. The presence of lead in small quantities (0·2–1·5%) in zinc is not very harmful, but with more than 2–3% of lead, zinc becomes brittle and difficult to roll into sheets. Iron rarely occurs in greater proportion than 0·2% and in such amount is not injurious, but in greater quantity it renders the metal hard and brittle. Cadmium also is always present in small proportion (0·01–0·1%) and is not deleterious unless the zinc is to be used for making zinc white. Tin is found only in remelted zinc. Arsenic, antimony and sulphur are usually found in traces, but if together they exceed 0·1% the metal is very brittle; a similar effect is exerted by copper to the extent of 0·5%. Carbon and silicon, which may sometimes be present in small proportions, have no appreciable injurious action.

The compositions of various refined zincs of commerce are as follows (Schnabel, Nissenson, Hollard):

TABLE XXVIII

**Composition of Zincs**

| Source. | Zn[1] | Pb | Fe | Cd | Ag | Cu | Sb | As | S | Si | C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Upper Silesia I | 98·782 | 1·118 | 0·024 | 0·012 | — | — | 0·022 | — | — | — | — |
| Upper Silesia II | 98·930 | 1·000 | 0·030 | 0·018 | — | — | — | — | — | — | — |
| Pulaski (U.S.) Bertha Spelter | 99·981 | — | 0·019 | — | — | — | — | — | — | — | — |
| Vieille Montagne Font d'Art | 98·904 | 1·070 | 0·016 | 0·010 | — | — | — | — | — | — | — |
| Vieille Montagne V.B.M. extra | 99·757 | 0·192 | 0·049 | trace | — | 0·002 | — | — | — | — | — |
| — — — I | 98·752 | 1·1524 | 0·0073 | 0·0705 | 0·0002 | trace | 0·0020 | 0·0015 | 0·0035 | 0·0022 | 0·0075 |
| — — — II | 99·868 | 0·1094 | 0·0065 | 0·0075 | trace | 0·0005 | 0·0018 | 0·0005 | 0·0005 | 0·0035 | 0·0006 |

## ZINC DUST

Commercial zinc dust constitutes a mixture of very finely divided zinc mixed with zinc oxide and variable proportions of cadmium, iron, lead, arsenic, carbon, etc., and is used as a reducing agent. It is usual to determine its reducing power towards solutions of potassium dichromate or ferric salts; in some cases, however, the volume of hydrogen obtained under the action of dilute hydrochloric acid is measured, the quantity of zinc present and hence the commercial value being deduced therefrom.

**1. Determination of the Reducing Power.**—*Reagents:* N/2-potassium dichromate (24·54 grams per litre) and N/2-thiosulphate.[2]

*Procedure.* 1 gram of the sample, 100 c.c. of the dichromate solution and 10 c.c. of dilute sulphuric acid (1 : 3) are shaken for 5 minutes in a

[1] By difference.

[2] For the titration of thiosulphate solution, *see* Chrome Steels.

bottle holding about 200 c.c. and fitted with a ground stopper. After addition of a further quantity of 10 c.c. of dilute sulphuric acid, the shaking is continued for 10–15 minutes—until all the zinc is dissolved. The bottle is emptied and washed into a half-litre measuring flask and made up to volume. 100 c.c. of the solution are acidified with 5 c.c. of hydrochloric acid (D = 1·10) and treated with 10 c.c. of 10% potassium iodide solution, the iodine separated being titrated with sodium thiosulphate and starch paste. The difference in c.c. between the volumes of dichromate and thiosulphate, multiplied by 0·01635, gives the amount of zinc in 0·2 gram of the sample.

***

Commercial zinc dust contains 80–90% Zn, 9–10% ZnO, 1·5–2% Pb, and small quantities of copper, cadmium, arsenic, antimony, iron, sulphur, silica, carbon, etc., and, sometimes, of calcium and magnesium oxides.

## LEAD AND ITS ALLOYS

Lead is largely used as such and also enters into the composition of numerous alloys.

Methods will be given here for the analysis of commercial lead and of hard lead, alloys of lead with tin and antimony (solder, white antifriction metal, white metal for fittings, etc.) being treated under tin and its alloys.

### LEAD

The analysis of commercial lead consists in determining the impurities present (silver, copper, bismuth, cadmium, arsenic, antimony, iron, nickel, cobalt, zinc and manganese). These impurities are, however, present in very small proportions (refined lead contains, indeed, 99·96–99·99% Pb), and it is therefore necessary to employ large quantities of the sample and to conduct all the analytical operations with the greatest precision.

In a 1·5-litre beaker, 200 grams of the metal are gently heated with a mixture of 500 c.c. of nitric acid (D 1·2) and 500 c.c. of water. After standing for about 12 hours, the liquid is filtered, the insoluble residue (lead antimonate) being collected on a small filter, washed, placed in a porcelain crucible and kept apart (residue *a*).

The filtrate is treated with 62–63 c.c. of concentrated sulphuric acid and left to cool and settle, the clear supernatant liquid being siphoned into a 3-litre beaker. The residue is shaken with 200 c.c. of water acidified with nitric acid, allowed to settle and the supernatant liquid added to the first solution ; to ensure complete washing, this operation should be repeated three or four times.

The liquid freed from lead sulphate is then rendered alkaline with ammonia and treated with 25–50 c.c. of colourless ammonium sulphide. Together with small quantities of lead which have passed into solution, the copper, silver, bismuth, iron, etc., are precipitated as sulphides, whilst the arsenic and antimony remain in solution in the alkaline sulphide. After remaining

for 2–3 hours on the water-bath, the liquid is filtered and the precipitate washed with water containing a little ammonium sulphide and added to the residue in the porcelain crucible (residue *a*), which is then carefully ignited. The oxides thus obtained are fused with sodium carbonate and sulphur (*see* Gravimetric Analysis of Ordinary Bronzes), the fused mass being extracted with water and the solution reduced with sulphite and filtered. The filtrate is added to the alkaline sulphide solution and the whole used for the determination of the *antimony* and *arsenic* (*see* 3) ; on the filter the other impurities remain as sulphides.

The precipitate thus obtained is dissolved in nitric acid (1 vol. of nitric acid, D = 1·2, and 2 vols. of water) and the liquid evaporated with a slight excess of sulphuric acid to eliminate the small quantities of lead still present and to expel the nitric acid (excess of sulphuric acid is necessary to keep the bismuth in solution) ; the residue is taken up in a little water, filtered and treated with hydrogen sulphide. *Bismuth, silver, cadmium* and *copper* sulphides are precipitated (*see* 1), whilst *nickel, cobalt, iron, zinc* and *manganese* remain in solution (*see* 2).

**1. Determination of the Bismuth, Silver, Cadmium and Copper.** —The sulphides precipitated with hydrogen sulphide are dissolved in nitric acid and the solution evaporated in presence of sulphuric acid.

(*a*) DETERMINATION OF THE BISMUTH. The residue is dissolved in a little water, almost neutralised with pure sodium hydroxide, treated with sodium carbonate in slight excess and with a little potassium cyanide and gently heated. If bismuth is present, a white precipitate is obtained, this being filtered off, well washed and dissolved in a little nitric acid. The bismuth is then precipitated with a slight excess of ammonia, the precipitate being washed and dissolved in nitric acid and the solution evaporated in a tared porcelain crucible ; the residue is ignited gently and weighed : $Bi_2O_3 \times 0{\cdot}8965 = Bi$.

(*b*) DETERMINATION OF THE SILVER.[1] The filtrate from the treatment with sodium carbonate and potassium cyanide is treated with a little more potassium cyanide and a few drops of sodium sulphide, the silver and cadmium being precipitated as sulphides, while any copper present remains in solution. The precipitate is collected, washed, dissolved in nitric acid and the silver precipitated as chloride by addition of a few drops of dilute hydrochloric acid : $AgCl \times 0{\cdot}7526 = Ag$.

(*c*) DETERMINATION OF THE CADMIUM. The filtrate from the silver chloride is evaporated almost to dryness and treated at the boiling point with sodium carbonate. The precipitate formed is collected, washed with hot water, dissolved in a little nitric acid, evaporated in a tared porcelain crucible, gently ignited and weighed : $CdO \times 0{\cdot}8754 = Cd$.

(*d*) DETERMINATION OF THE COPPER. The filtrate from the silver and cadmium sulphides (*see b*) is treated with a little sulphuric and nitric acids and a few drops of hydrochloric acid and evaporated to dryness. The residue is dissolved in water and the copper determined electrolytically or gravimetrically.

[1] The silver is more exactly determined directly by cupellation (*see* Silver and its Alloys).

**2. Determination of the Nickel, Cobalt, Iron, Zinc and Manganese.**—The filtrate from the bismuth, silver, cadmium and copper sulphides is collected in a flask, rendered slightly ammoniacal and treated with 3 c.c. of ammonium sulphide. The flask is filled with water and left closed for 24 hours, after which the precipitate is collected, washed with hot water containing a few drops of ammonium sulphide and treated on the filter with a mixture of 5 parts of saturated hydrogen sulphide solution and 1 part of hydrochloric acid (D 1·2). The iron, zinc and manganese sulphides are dissolved and these metals are determined as in (*b*) and (*c*); nickel and cobalt sulphides remain on the filter and are determined as in (*a*).

(*a*) DETERMINATION OF THE NICKEL AND COBALT. The nickel and cobalt sulphides, which have remained undissolved, are ignited and weighed as oxides, which are then dissolved in aqua regia, the solution rendered alkaline with ammonia, and the nickel precipitated with dimethylglyoxime (*see* Argentan).

(*b*) DETERMINATION OF THE IRON. The hydrogen sulphide is expelled by boiling from the hydrochloric acid solution containing the iron, zinc and manganese, oxidation being effected by a few drops of nitric acid and the liquid made alkaline with ammonia. The precipitated ferric hydroxide is collected, washed and dissolved in hydrochloric acid, the iron being then reprecipitated with ammonia and weighed as ferric oxide: $Fe_2O_3 \times 0{\cdot}6994 = Fe$.

(*c*) DETERMINATION OF THE ZINC. The filtrates from the iron precipitate are together rendered alkaline with ammonia and treated in a flask with 2–3 c.c. of ammonium sulphide, the flask being then filled with water, stoppered and left for 24 hours. The zinc and manganese sulphides are then collected, washed and treated on the filter with dilute acetic acid, which dissolves only the manganese sulphide. The residue, consisting of zinc sulphide, is dissolved on the filter by dilute hydrochloric acid and the solution evaporated to dryness in a tared crucible. The residue is mixed with an aqueous suspension of a little pure mercuric oxide free from alkali, evaporated to dryness, heated gently over a naked flame to eliminate the mercury, ignited over a blowpipe flame and weighed: $ZnO \times 0{\cdot}8034 = Zn$.

(*d*) DETERMINATION OF THE MANGANESE. The acetic acid solution of the manganese is concentrated and treated with ammonia and hydrogen peroxide to precipitate the manganese, the precipitate being collected, washed, dried, ignited and weighed: $Mn_3O_4 \times 0{\cdot}7203 = Mn$.

**3. Determination of the Arsenic and Antimony.**—(*a*) DETERMINATION OF THE ARSENIC. The alkaline sulphide solution obtained as described on p. 245 is acidified with acetic acid and heated for 3–4 hours on the water-bath, the arsenic and antimony sulphides and sulphur which separate being filtered off. The precipitate is washed with saturated hydrogen sulphide solution slightly acidified with acetic acid, dried, freed from sulphur by means of carbon disulphide, filtered, and the arsenic and antimony sulphides dissolved in hydrochloric acid and potassium chlorate. The liquid is filtered through a small filter, and the filtrate treated with 0·5 gram of tartaric acid and neutralised with ammonia; the solution, which should occupy about 20 c.c., is then treated with 10 c.c. of concen-

trated ammonia and 1–2 c.c. of magnesia mixture. After about 24 hours, the magnesium ammonium arsenate is collected on a filter, transformed by ignition into pyroarsenate and weighed: $Mg_2As_2O_7 \times 0{\cdot}4827 = As$.

(*b*) DETERMINATION OF THE ANTIMONY. The filtrate from the magnesium ammonium arsenate is treated with ammonium sulphide and acidified slightly with sulphuric acid. The antimony is thus precipitated as sulphide, which is dissolved in ammonium sulphide, the solution being evaporated in a tared porcelain crucible, oxidised with nitric acid, calcined gently and weighed: $Sb_2O_4 \times 0{\cdot}7898 = Sb$.

***

The refined lead of commerce, especially that destined for making electrical accumulator plates, is a very pure metal, containing 99·96–99·99% Pb.

The compositions of samples of lead of different origins are as follows (Schnabel, Hollard, Hampe):

TABLE XXIX

**Composition of Samples of Lead**

| Origin. | Pb | Sb | Ag | Cu | Zn | Fe | Bi | As | Cd | Ni | Mn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pertusola I. | 99·9915 | 0·0050 | 0·001 | 0·0003 | 0·0006 | 0·0016 | — | — | — | — | — |
| Pertusola II | 99·9937 | 0·0013 | 0·0006 | — | 0·00085 | 0·0014 | 0·0021 | — | — | — | — |
| Monteponi (Sardinia) | 99·99 | 0·0030 | 0·0010 | 0·0005 | 0·0021 | 0·0047 | 0·0007 | — | — | — | — |
| Pennsylvania (Lead Co.) | 99·9924 | 0·0012 | 0·0002 | 0·0002 | 0·0007 | 0·0017 | 0·0030 | — | — | — | 0·0002 |
| Germany | 99·9852 | 0·0044 | 0·0006 | 0·0007 | 0·0005 | 0·0011 | 0·0073 | — | trace | trace | — |
| | | | | | Zn,Ni,Co | | | | | | |
| Spain (Penarroya) | 99·989 | 0·003 | — | trace | 0·005 | 0·012 | 0·091 | — | — | — | —[1] |
| Sweden | 99·9575 | 0·0040 | trace | 0·0018 | 0·0002 | 0·0015 | 0·0350 | trace | trace | — | — |

## HARD LEAD

Hard lead or antimonial lead is an alloy of lead and antimony containing small quantities of copper and tin and sometimes also iron, nickel, cadmium, arsenic, etc., and serves for making type, the plates of certain forms of electric accumulators and cast ornamental articles, and as anti-friction metal, etc.

The essential determinations to be made on these alloys for a complete analysis (*see B*) are those of the lead, antimony, copper and tin, determinations of iron, nickel, arsenic, etc., not being always necessary. Often, however, determinations of certain elements only are required (*see* Partial Analysis).

### *A.* Partial Analysis

For special purposes, determinations of the copper and tin alone are required.

**1. Direct Determination of the Copper.**—*See* Direct Determination of Copper in White Metal.

**2. Direct Determination of the Tin.**—From 2 to 4 grams of the sample in fine filings are heated to boiling, in an inclined long-necked flask covered with a funnel, with 20 c.c. of conc. sulphuric acid until the lead sulphate separating appears perfectly white. The cold mass is treated with 2–3 grams of tartaric acid dissolved in a little water and the whole introduced quantitatively into a 100 c.c. measuring flask, made up to volume, mixed and filtered through a dry, pleated filter. 50 c.c. of the filtrate are rendered alkaline with ammonia, heated gently with 5 grams of oxalic acid and the clear solution treated with 5 grams of ammonium oxalate, diluted to about 150 c.c. and kept gently *boiling* during the passage of hydrogen sulphide to precipitate the antimony and copper. After about an hour, the liquid is allowed to cool a little and filtered, 1% oxalic acid solution saturated with hydrogen sulphide being used for washing.

The filtrate is boiled for a short time with 30 c.c. of hydrochloric acid and 20 grams of ammonium oxalate to expel the hydrogen sulphide. After being allowed to cool somewhat, the liquid is treated with a few drops of hydrogen peroxide, heated a short time, made up to about 300 c.c., cooled to 50–60° and electrolysed—turbid with sulphur as it often is—to determine the tin: coppered Winkler cathode, spiral Winkler anode, $ND_{100}$ = 1 amp., temperature about 50°, duration (0·1–0·3 gram Sn) 4–5 hours.

Since the antimony and copper sulphides precipitated may retain small amounts of tin, for an exact analysis the precipitation should be carried out twice. These sulphides are, therefore, dissolved in the hot in a mixture of 10–15 c.c. of conc. hydrochloric acid, 10–15 c.c. of 10% ammonium chloride solution and a few crystals of potassium chlorate, the solution being diluted with a little water, filtered, rendered alkaline with ammonia, treated with 5 grams of oxalic acid and 5 grams of ammonium oxalate, diluted to 100 c.c. and subjected at the boiling point to a current of hydrogen sulphide. After about an hour, the liquid is filtered and the precipitate washed with the oxalic solution saturated with hydrogen sulphide. The two filtrates are united and the solution—concentrated if necessary—or an aliquot part of it used for the electrolytic determination of the tin.

## *B.* Complete Analysis

In a 250 c.c. measuring flask, 2·5 grams of the sample in fine filings are gently heated with 15 c.c. of water and 10 grams of powdered tartaric acid until the latter dissolves, 4–5 c.c. of nitric acid being added gradually and with shaking, and the liquid left until the metal is completely dissolved. 4 c.c. of conc. sulphuric acid are then added and the cooled liquid made up to volume and mixed, and, after a brief stand, filtered through a tared Gooch crucible into a dry vessel. Of the filtrate 50 c.c. (= 0·5 gram of alloy) are used for the determination of the *antimony* (*see* 2) and 100 c.c. (= 1·0 gram of alloy) for that of the *tin* and *copper* (*see* 3).

**1. Determination of the Lead.**—When these two portions of the filtrate are removed, the whole of the lead sulphate in the 250 c.c. flask is transferred to the Gooch crucible and is washed, first with a mixture of 250 c.c. of water, 10 grams of tartaric acid and 4 c.c. of sulphuric acid and then with

95% alcohol until the reaction is neutral, and subsequently dried, heated in an air-bath, cooled in a desiccator and weighed : $PbSO_4 \times 0{\cdot}6831 = Pb$.

**2. Determination of the Antimony.**—The 50 c.c. of solution taken is concentrated to 20–30 c.c., neutralised with 50% sodium hydroxide solution, an excess of 3–4 c.c. of the latter and 30 c.c. of sodium sulphide solution (D 1·225) added and the liquid heated and, after some time, filtered to remove the copper sulphide, etc., directly into a tared Classen capsule ; the precipitate is washed with hot water in which a little sodium sulphide is dissolved. The filtrate is treated with 50 c.c. of sodium sulphide and 5–6 grams of pure potassium cyanide, mixed and electrolysed to determine the antimony, $ND_{100} = 0{\cdot}15$–$0{\cdot}18$ amp., voltage = 1–1·2, duration (0·1–0·15 gram Sb) 15–18 hours. When the deposition is complete, the capsule is emptied, thoroughly washed with water, alcohol and ether, dried at 70° and weighed.

**3. Determination of the Tin and Copper.**—The 100 c.c. of solution taken is rendered slightly alkaline with ammonia, treated with 5 grams of oxalic acid, heated to obtain a clear solution, treated with 7 grams of ammonium oxalate, and kept boiling for about an hour while a stream of hydrogen sulphide is passed to precipitate the antimony and copper. When the liquid has cooled somewhat in the current of hydrogen sulphide, it is filtered into a half-litre beaker, the filter being washed with a hot 1% oxalic acid solution saturated with hydrogen sulphide.

(*a*) DETERMINATION OF THE TIN. The filtrate is treated with 30 c.c. of conc. hydrochloric acid and 20 grams of ammonium oxalate and boiled for a short time to expel hydrogen sulphide. After the liquid has cooled somewhat, a few drops of 30% hydrogen peroxide are added and the solution heated for a little while, made up to 300 c.c., cooled to 40–45° and—often turbid with sulphur—electrolysed to determine the tin : coppered Winkler cathode, spiral anode, $ND_{100} = 1$ amp., voltage = 3–4, temperature = 40–50°, duration (0·1–0·3 gram Sn) = 4–5 hours (*see also* Electrolytic Determination of Tin in Ordinary Bronzes).

(*b*) DETERMINATION OF THE COPPER. The precipitated copper and antimony sulphides, which have been filtered off, are heated gently with 1% sodium hydroxide solution and filtered, the filter being thoroughly washed with water faintly alkaline with sodium hydroxide ; the copper sulphide remains undissolved. The filter-paper and precipitate are dried in a small dish, the filter incinerated, the residue dissolved in nitric acid, and the copper determined in this solution by the usual method (*see* Determination of Copper in Ordinary Brass).[1]

**4. Determination of the Iron, Nickel and Zinc.**—5 grams of the sample are treated with nitric acid (D = 1·2), the solution being left on the water-bath for a short time and then filtered ; the filtrate is treated with excess of sulphuric acid and evaporated to complete elimination of the nitric acid. The residue is taken up in water, filtered, treated with hydrogen sulphide and filtered again, the filtrate being used for the determination of the iron, zinc and nickel as in argentan.

[1] It should be borne in mind that cadmium may sometimes be present as well as copper.

**5. Determination of the Arsenic.**—*See* Copper.

***

Hard lead contains variable quantities of antimony (usually 10–25%) and may contain small amounts of copper, tin, iron, nickel, arsenic, etc.

The following table contains the results of analysis of samples of hard lead, obtained directly, from o res of lead and antimony (Schnabel) :

TABLE XXX

**Composition of Hard Leads**

| Source. | | Pb | Sb | Cu | As | Sn |
|---|---|---|---|---|---|---|
| Oberharz | I . . . . . | 81·71 | 17·69 | 0·62 | — | — |
| | II . . . . . | 82·44 | 16·90 | 0·68 | — | — |
| | III . . . . . | 82·08 | 17·34 | 0·62 | — | — |
| Freiberg . . . . . | | — | 15 | — | 2·5 | 0·3 |

## ANTIMONY AND ITS ALLOYS

Owing to its brittleness, antimony is rarely used as such, but it forms part of many industrial alloys, such as white bearing metals, type metal, etc.

Methods for determining the impurities commonly accompanying commercial antimony are therefore described, since the value depends on the purity.

Lead-antimony alloys are treated under lead, while alloys of antimony with tin alone or with tin and lead together (white metals) are dealt with along with tin.

### ANTIMONY

Analysis of commercial antimony is generally limited to the determination of its commoner impurities : lead, bismuth, copper, iron, arsenic and sulphur.

10 grams of the finely powdered sample are treated with aqua regia (140 c.c. HCl, 20 c.c. $HNO_3$) diluted with an equal volume of water, the solution thus obtained being treated with 60–70 c.c. of 50% tartaric acid solution, then made alkaline with concentrated sodium hydroxide solution and subjected to a current of hydrogen sulphide. The separation of the sulphides is facilitated by heating on a water-bath, the precipitate being filtered off and washed once or twice with hot water containing a few drops of sodium sulphide. The precipitate is then dissolved in a little hydrochloric acid containing bromine and 1–2 drops of tartaric acid added to the solution, which is rendered alkaline with sodium hydroxide and again precipitated with hydrogen sulphide to ensure the complete elimination of the antimony. After a short rest on the water-bath, the liquid is filtered

and the sulphides washed thoroughly with hot water containing a little sodium sulphide and dissolved in nitric acid (D 1·2).

**1. Determination of the Lead.**—The nitric acid solution is evaporated in presence of excess of sulphuric acid until white fumes appear, taken up in a little water and mixed with a few c.c. of 95% alcohol; after some time, the lead sulphate separated is collected in a Gooch crucible as indicated for the determination of lead in ordinary brasses (*see* p. 226).

**2. Determination of the Bismuth.**—The liquid freed from lead sulphate is heated to expel the alcohol and treated with hydrogen sulphide to precipitate the bismuth and the copper. The precipitate is filtered off, washed with hydrogen sulphide solution acidified with a few drops of sulphuric acid, and dissolved in a little nitric acid (D 1·2). The solution is evaporated in presence of sulphuric acid, taken up in a little water, neutralised almost completely with sodium hydroxide, and heated gently with a slight excess of sodium carbonate and a little potassium cyanide. The bismuth precipitate thus obtained is collected on a filter, washed, dissolved in nitric acid and again precipitated with ammonia under the conditions indicated for the determination of bismuth in lead.

**3. Determination of the Copper.**—The filtrate from the bismuth—after treatment with sodium carbonate and potassium cyanide (*see* 2)—is acidified with nitric acid and a few drops of sulphuric acid, evaporated to dryness, taken up in hot water and the copper in the solution determined by the usual methods.

**4. Determination of the Iron.**—The filtrate obtained after removal of the bismuth and copper as sulphides (*see* 2) contains all the iron, which is determined by expelling the excess of hydrogen sulphide, oxidising with nitric acid and precipitating with ammonium chloride and ammonia.

**5. Determination of the Arsenic.**—*See* Determination of Arsenic in Copper.

**6. Determination of the Sulphur** (Hollard and Bertiaux).—5 grams of the sample are treated with nitric acid to which sufficient hydrochloric acid is added to give a clear solution. The liquid is evaporated to dryness, taken up again in nitric acid and evaporated several times with nitric acid to expel the hydrochloric acid completely. The residue is finally treated with water faintly acidified with nitric acid and the solution filtered and the residue washed with water. To the filtrate sufficient ammonia is added to redissolve the antimony oxide at first separating, excess of nitric acid being then added and the liquid filtered. In the clear solution the sulphuric acid, formed by oxidation of the sulphur in the sample, is precipitated by means of barium nitrate.

***

Commercial antimony generally contains small quantities of lead, copper, iron, sulphur and, sometimes, bismuth, nickel and cobalt. Pure antimony is silvery white, but the commercial metal has a slightly bluish tint owing to the impurities present. It exhibits a marked tendency to crystallise and, indeed, usually has a crystalline structure, which is manifested even on the outside by large crystals resembling fern leaves, these being regarded—not always with reason—as a sign of the purity of the metal.

The compositions of various samples of antimony of different origin are as follows (Schnabel) :

TABLE XXXI

**Results of Analyses of Antimony**

| Origin. | Sb | Cu | Fe | Pb | As | Bi | S | Ni + Co |
|---|---|---|---|---|---|---|---|---|
| Hungary (Liptau) . . | 98·27 | 0·54 | 0·63 | — | — | 0·36 | — | — |
| California I . . . | 98·34 | 0·021 | 0·144 | 0·410 | 1·008 | — | 0·064 | 0·013 |
| California II . . . | 99·081 | 0·052 | 0·039 | 0·538 | 0·036 | — | 0·254 | trace |
| Of various origins (analysis by Hilmy) I | 98·98 | 0·01 | 0·35 | 0·34 | 0·09 | — | 0·23 | — |
| Of various origins (analysis by Hilmy) II | 98·87 | 0·02 | 0·16 | 0·73 | 0·09 | — | 0·11 | — |

## TIN AND ITS ALLOYS

Tin is one of the most important metals, being largely used as such and also as a constituent of numerous industrial alloys.

Methods will be given here for the determination of elements occurring in commercial tin as impurities, for the analysis of tin-plate and the more important tin alloys (phosphor-tin, solder, white antifriction metals, type metal and metal for fittings).

Alloys of tin with copper (bronzes) are considered along with copper.

### TIN

Commercial tin is usually contaminated by small quantities of lead, copper, iron, bismuth, antimony, sulphur, and arsenic and sometimes traces of molybdenum, tungsten, zinc, manganese, nickel, chromium, etc. The more important determinations are those of lead, bismuth, copper, iron, antimony, arsenic and sulphur, qualitative tests for the other elements being sufficient.

**1. Determination of the Lead, Bismuth, Copper and Iron.**— According to the greater or less degree of impurity, from 10 to 20 grams of the sample, flattened on an anvil or in a small rolling mill and cut up fine, are heated gently on a water-bath with aqua regia (1 vol. of nitric acid with 5 vols. of hydrochloric acid ; 10 grams of the sample require 140 c.c., and 20 grams, 180 c.c.). When the metal is completely attacked, the liquid is allowed to cool and treated, according to the weight of sample taken, with 25–35 grams of tartaric acid ; the latter is dissolved by gentle heating, the liquid then rendered alkaline with 20% sodium hydroxide solution, and 25 c.c. of 2% sodium sulphide solution added with continual shaking. Separation of the lead, bismuth, copper and ferric sulphides is facilitated by heating for some time on the water-bath, the precipitate being ultimately filtered off and washed with dilute sodium sulphide solution.

(*a*) DETERMINATION OF THE LEAD. The precipitate obtained with

sodium sulphide is dissolved in a little nitric acid (D 1·2) and the solution evaporated in presence of sulphuric acid until white fumes appear; the residue is treated with water, alcohol added and the lead sulphate collected on a closely-woven filter paper. As it may contain small quantities of tin, the precipitate is redissolved in ammonium acetate solution and the lead reprecipitated with hydrogen sulphide and converted into sulphate, which is collected on a Gooch crucible as usual (*see* Gravimetric Determination of Lead in Ordinary Brass).

(*b*) DETERMINATION OF THE BISMUTH AND COPPER. The alcohol is expelled from the liquid separated from the first lead sulphate precipitate and the bismuth and copper precipitated with hydrogen sulphide and determined as in the analysis of antimony.

(*c*) DETERMINATION OF THE IRON. The iron is determined as oxide in the filtrate from the bismuth and copper sulphides (*see* Determination of Iron in Antimony).

**2. Determination of the Antimony.**—10 grams of the sample are treated with 100 c.c. of hydrochloric acid (D 1·124) and potassium chlorate, the chlorine eliminated by boiling, the volume made up to about 250 c.c., and, while the liquid is heated on the water-bath, 6 grams of pure reduced iron added in small quantities to displace the copper and antimony. The separated metals, together with the small amount of undissolved iron, are filtered off and washed on the filter with dilute hydrochloric acid until the filtrate no longer gives the reaction for tin with mercuric chloride. The separated metals are then dissolved in hydrochloric acid and potassium chlorate, the excess of chlorine expelled by boiling, the copper and antimony precipitated with hydrogen sulphide and the precipitate well washed and treated with 30 c.c. of sodium sulphide solution (D 1·225) to dissolve the antimony sulphide. The liquid is filtered directly into the Classen dish, the filter washed with 50 c.c. of the sodium sulphide solution, and the filtrate, with the addition of 5–6 grams of potassium cyanide, electrolysed to determine the antimony (*see* Determination of Antimony in Hard Lead).

**3. Determination of the Arsenic.**—(*a*) 10 grams of the sample are dissolved in a solution of 100 grams of ferric chloride in 100 c.c. of water, excess of conc. hydrochloric acid being added and the arsenic distilled in the ordinary way (*see* Determination of Arsenic in Iron).

(*b*) 10 grams of the sample are dissolved in hydrochloric acid containing potassium chlorate, the chlorine being expelled by boiling, and the cold liquid mixed with one-third of its volume of conc. hydrochloric acid and hydrogen sulphide passed through it for some hours. The arsenic sulphide thus precipitated is filtered off on an asbestos filter (Gooch crucible), washed with conc. hydrochloric acid and then with boiled water and dissolved in ammonia; the solution is evaporated in a dish and the residue dissolved in conc. nitric acid, made strongly alkaline with ammonia and the arsenic precipitated with magnesia mixture and alcohol. The precipitate is collected, washed, transformed into pyroarsenate and weighed.

**4. Determination of the Sulphur.**—*See* Determination of Sulphur in Iron.

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Tin of good quality should be white and lustrous and of crystalline structure and, if in rods, it should give the characteristic crackling when bent in different directions. It should not contain more than 0·1% of sulphur and arsenic together, or more than 0·01% of bismuth, or more than 1% of total impurities.

The compositions of tins of different origin are as follows (Hollard, Schnabel):

TABLE XXXII

**Composition of Samples of Tin**

| Source. | | Sn | Pb | Fe | Cu | Bi | Sb | As |
|---|---|---|---|---|---|---|---|---|
| Straits Settlements | Banka | 99·961 | 0·014 | 0·019 | 0·006 | — | — | — |
| | Malacca | 99·805 | — | 0·020 | 0·072 | — | 0·060 | 0·043 |
| | Pulo Brani | 99·76 | 0·02 | 0·14 | — | — | 0·07 | — |
| China (Hong-Kong) | | 98·928 | 0·833 | 0·037 | 0·040 | — | 0·044 | 0·118 |
| England | | 99·76 | — | trace | 0·24 | — | — | — |
| Germany | I | 99·336 | — | — | 0·480 | 0·060 | 0·545 | 0·079 |
| | II | 99·594 | — | trace | 0·406 | — | — | trace |

## TIN-PLATE

With commercial tin-plate the most important determination to be made is that of the tin, the thickness of the layer of this metal determining the value; next comes the determination of the lead, which gives an indication of the quality of the tin used. For these two determinations *see* 1.

Sometimes, however, for certain purposes (hygienic, for instance) determination of the lead alone is of interest, it being desired to ascertain if the tinning has been done with commercial tin or with an alloy of lead and tin. The determination of the lead alone is described in 2.

**1. Determination of the Tin and Lead.**—From 1 to 2 sq. dms. of the tin-plate [1]—taken from the middle of the plate, since the tinning is often irregular at the edges—is measured exactly, de-fatted with ether or benzene and weighed, so that the results may be referred to the weight as well as the surface of the sample. The measured portion is cut into small squares of 1–2 cm. side, these being heated to boiling for 5 minutes in a covered beaker with 50 c.c. of 10% hydrochloric acid (25–30 c.c. conc. hydrochloric acid diluted to 100 c.c. with water). The hydrochloric acid solution is decanted into a 300 c.c. measuring flask and the metal boiled for 5 minutes with another 50 c.c. of the acid, this being decanted off and, if necessary, the residue treated a third time; the colour of the metal should be a uniform iron-grey when all the tin is dissolved. Tin and lead are easily dissolved in the hot by hydrochloric acid of this concentration, while the iron is attacked but little.[2] The residue is washed with a little water and this decanted into the 300 c.c. flask, the contents of which are rendered

[1] With a very irregular sample a larger quantity is taken.

[2] If the tin-plate is very rich in lead, a few drops of nitric acid are added to the hydrochloric acid.

slightly alkaline with ammonia, treated with 45–50 c.c. of ammonium sulphide [1] prepared from ammonia of D = 0·910, cooled, made up to volume and filtered through a dry filter. The alkaline sulphide solution serves for the determination of the tin and the precipitate, consisting of lead and iron sulphides, for determining the lead.

*A*. DETERMINATION OF THE TIN. 1. *Electrolytically*. Either stationary or rotating electrodes may be used.

(*a*) Rotating electrodes. 100 c.c. of the filtrate are treated in a 300 c.c. beaker with 20–30 c.c. of 40% sodium sulphite solution to reduce the polysulphides, made up to about 200 c.c. and electrolysed at 60°. Coppered and then tinned Winkler cathode [2]; spiral anode, 1000 revs. per minute; temperature, 60°; $ND_{100}$, 3–3·5 amp.; voltage, 5-6; duration, 15–20 minutes.

When the electrolysis is complete, the rotation of the anode is suspended and, without interrupting the current, the electrolytic beaker replaced by one filled with water; after some time, the cathode is detached, washed successively with water, alcohol and ether, dried at 70° and weighed. The weight found, multiplied by 3, gives the tin contained in the sample taken.

When rotating electrodes are used, the determination of tin in tin-plate occupies not longer than an hour.

(*b*) Stationary electrodes. In a ½-litre conical flask, 100 c.c. of the alkaline sulphide filtrate are treated, under a draught hood, with a little potassium cyanide to reduce the polysulphides, and hydrochloric acid diluted with an equal volume of water added until the reaction is acid, the flask being kept covered with a funnel and shaken meanwhile. When evolution of gas ceases, the liquid is boiled for some time with 25 c.c. of conc. hydrochloric acid to dissolve the tin sulphide which separates and to coagulate the sulphur. After addition of 25 grams of ammonium oxalate and dilution to 250 c.c., the liquid is electrolysed: coppered Winkler cathode; Winkler spiral anode; $ND_{100} = 1$ amp.; voltage = 3–4; temperature, 60°; duration (for 0·1–0·5 gram Sn), 4–5 hours (*see also* Electrolytic Determination of Tin in Ordinary Bronzes). Multiplication by three of the tin found gives the amount in the sample taken.

2. *Gravimetrically*. In a ½-litre conical flask, 50 or 100 c.c. of the alkaline sulphide filtrate (*see* 1, p. 254) are diluted with water and acetic acid added until the reaction is faintly acid, the tin being thus precipitated as sulphide. After standing overnight, the precipitate is filtered off, washed with 10% ammonium acetate solution and dried at 100-120°. The filter and precipitate are introduced into a tared porcelain crucible, the filter-paper incinerated with addition of a few crystals of ammonium carbonate and then ignited until the stannic sulphide is completely converted into the white oxide and weighed: $SnO_2 \times 0{\cdot}7881 = Sn$.

[1] In presence of copper it is convenient to use sodium sulphide, but in such case the rapid determination of the tin with rotating electrodes cannot be carried out.

[2] For the coppering of the electrode, *see* p. 225. For the subsequent tinning, the following solution is employed: 3–4 grams of stannic ammonium chloride are dissolved in 150 c.c. of cold water to which are added 150 c.c. of saturated ammonium bioxalate solution. The cathode is immersed in this solution and the current passed for some minutes: $ND_{100} = 0{\cdot}2$–$0{\cdot}5$ ampere.

*B.* DETERMINATION OF THE LEAD. 1. *Electrolytically.* The lead and iron sulphides (*see* p. 255) are washed with water containing a little ammonium or sodium sulphide, and the filter and precipitate heated to boiling with 15–20 c.c. of nitric acid (D 1·2) in a small covered beaker. The solution is decanted through a filter and the residue boiled with 20–30 c.c. of the following mixture, which dissolves also any small amount of lead sulphate formed by oxidation of the sulphide: 40 c.c. of ammonia (D 0·923), 67 c.c. of nitric acid (D 1·332) and 5 grams of copper nitrate. The liquid is filtered, the filter washed with hot water acidified with nitric acid, and the filtrate made up to about 200 c.c. and electrolysed to determine the lead: Winkler cathode; matte gauze cylinder anode; ND = 0·3 amp.; voltage, 1·8–2 (*see also* Electrolytic Determination of Lead in Ordinary Brass).

When the deposition of the lead is complete, the anode is washed with water alone, dried at 200–220° and weighed: $PbO_2 \times 0{\cdot}866 = Pb$.

2. *Gravimetrically.* The lead and iron sulphides (*see* 1, p. 255) on the filter are well washed with water containing a little ammonium sulphide, dissolved in nitric acid (D 1·2) and filtered by decantation. The residue is again boiled twice with nitric acid and finally washed with water acidified with nitric acid. The nitric acid solution is evaporated with sulphuric acid until white fumes appear, and the residue, when cold, taken up in water, the lead being determined as sulphate as in the case of tin.

**2. Determination of the Lead alone.**—The surface of the tin-plate is scraped with a penknife so that as little as possible of the metal underneath is removed, about 1–1·5 gram of thin shavings being obtained; any particles of iron are removed with a magnet. The shavings are mixed in a covered beaker with 6 c.c. of fuming nitric acid (D 1·5), 3 c.c. of water being poured carefully down the side of the beaker so that the two liquids mix slowly and the action proceeds regularly. At the end of the action, the liquid is heated to boiling, diluted with 50 c.c. of boiling water and, when the liquid above the metastannic acid has become clear, filtered by decantation through a dense filter and washed by decantation with water slightly acidified with nitric acid.

In the filtrate the lead is determined either electrolytically or gravimetrically by the methods given for the analysis of alloys of lead and tin (*see* p. 259). When the lead is separated as peroxide or sulphate, the iron unavoidably present is determined in the residual liquid by precipitating with ammonium chloride and ammonia. Deduction of the weight of iron found from the total weight of the shavings gives the amount of lead-tin alloy taken for analysis, and to this the quantity of lead found is referred.

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Good tin-plate should exhibit a clean, smooth surface without spots or bubbles and with a uniformly thick layer of tin. It should have at least 0·25–0·3 gram of tin per sq. dm. (the best qualities have 0·6–0·7 gram per sq. dm.), and the tin used should not contain more than 1% of lead.

## PHOSPHOR-TIN
### (Tin phosphide)

The analysis of phosphor-tin, which is used especially for the preparation of phosphor-bronzes, includes:

**1. Determination of the Phosphorus.**[1]—The alloy is treated with hydrochloric acid and the phosphorus thus liberated as hydrogen phosphide, which is oxidised with bromine water and determined as phosphoric acid.

*Apparatus.* A flask of about 500 c.c. capacity furnished with a stopper through which pass (1) a tapped funnel for the introduction of the hydrochloric acid and (2) two tubes bent at right angles, one reaching almost to the bottom of the vessel and serving for the introduction of a stream of carbon dioxide into the apparatus, and the other to collect the gas evolved during the reaction. The latter tube communicates with three absorption bottles, two containing bromine water and a small quantity of bromine (a layer some millimetres deep) and the third bromine water alone.

*Procedure.* 2–5 grams of the alloy in small fragments are introduced into the flask and the latter stoppered and connected with the washing bottles, a current of carbon dioxide being passed for about five minutes to expel the air. From 50 to 100 c.c. of concentrated hydrochloric acid are then added, little by little, and when the attack is complete the liquid is heated to boiling and a current of carbon dioxide again passed to drive out the products of the reaction. The contents of the three bottles are washed into a beaker, the excess of bromine eliminated by boiling and the phosphoric acid precipitated either (1) as magnesium ammonium phosphate which, after standing, is filtered off, dried, ignited strongly and weighed: $Mg_2P_2O_7 \times 0{\cdot}2787 = P$,[2] or (2) with ammonium molybdate (*see* Iron, 4).

**2. Determination of the Tin.**—The hydrochloric acid solution is collected in a 500 c.c. measuring flask and made up to volume. An aliquot part, corresponding with 0·5–0·75 gram of the sample, is rendered alkaline with ammonia, the precipitate redissolved by addition of a little oxalic acid and the liquid boiled for a short time with 25 c.c. of hydrochloric acid, 25 grams of ammonium oxalate and a few drops of hydrogen peroxide, made up to about 250 c.c. and electrolysed at 40–50° to determine the tin (*see* Electrolytic Determination of Tin in Ordinary Bronzes).

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Commercial phosphor-tin or tin phosphide usually contains about 4% of phosphorus. The brand marked N.o contains about 5% P and N.1, 2·5%. Other products, however, contain only 1% or even less.

[1] W. Gemmell and S. L. Archbutt, *Journ. Soc. Chem. Industry*, 1908, XXVII, p. 427.

[2] If the sample contains arsenic, magnesium ammonium arsenate is precipitated with the magnesium ammonium phosphate. In this case the weighed precipitate is redissolved in hydrochloric acid, the solution reduced with sulphur dioxide and the arsenic precipitated with hydrogen sulphide.

## ALLOYS OF LEAD AND TIN

The lead-tin alloys are used for *soldering* and for many other purposes, such as making ornamental articles, statuettes, toys, tubes for paints and perfumery, tin-foil, etc.

In these alloys, the essential determinations are those of the lead and tin (*see* 1). Sometimes, however, for special products, the determination of the lead alone or of the tin alone is of interest (*see* 2), whilst in other cases, determination of the impurities (Cu, Sb, As, etc.) is desired (*see* White Metals).

**1. Determination of the Lead and Tin.**—About 1 gram of the alloy as filings is treated in a covered beaker with 6 c.c. of fuming nitric acid (D = 1·5) and 3 c.c. of water then poured carefully down the side of the beaker so that the two liquids mix slowly and the action proceeds slowly and regularly. When the action is complete, the liquid is heated to boiling, diluted with 50 c.c. of boiling water, and, when the liquid above the precipitated metastannic acid has become clear, filtered by decantation through a close filter-paper. The precipitate is washed by decantation with water slightly acidified with nitric acid, collected on the filter, washed with hot water [1] and treated as in *B*. The filtrate is utilised as in *A*.

*A*. Determination of the Lead.

1. *Electrolytically*. The filtrate is made up to volume and an aliquot part, containing about 0·2–0·25 gram of lead, is treated with 1–2 grams of pure copper dissolved in 10–15 c.c. of nitric acid, diluted to 200–250 c.c., and electrolysed at the ordinary temperature: Winkler anode; cylindrical gauze cathode; $ND_{100}$ = 0·3 amp.; voltage = 2–2·2; and duration, 10–15 hours.

When by raising the level of the liquid the deposition of the lead is found to be complete—even although copper may still remain in solution—the electrolytic beaker is replaced by another filled with distilled water, the current being maintained. After some time the anode coated with lead peroxide is detached, washed with water *alone* and dried at 200–220°. The factor for converting weight of peroxide into that of lead is 0·866, 0·865 or 0·8635 according as the amount of the peroxide is less than 0·1 gram, between 0·1 and 0·3 gram, or above 0·3 gram (Classen).

2. *Gravimetrically*. The filtrate is evaporated in presence of 3–4 c.c. of conc. sulphuric acid until white fumes appear. When cold, the liquid is taken up with 50 c.c. of water, heated gently and stirred, allowed to cool and treated with 15 c.c. of 95% alcohol. After 1–2 hours, the lead sulphate is collected in a Gooch crucible and weighed (*see* Gravimetric Determination of Lead in Ordinary Brass).

*B*. Determination of the Tin.

1. *Electrolytically*. The metastannic acid precipitate with the filter-

[1] When fuming nitric acid is used, the metastannic acid separating is practically free from lead (Busse: *Zeitschr. analyt. Chem.*, 1878, XVII, p. 53). If it is desired to determine the minimal quantities of lead retained in the metastannic acid, the methods indicated for the determination of tin in ordinary bronzes (*see* p. 232) may be used.

paper is treated in a small beaker with 2–3 c.c. of 10% sodium hydroxide solution and 10–15 c.c. of sodium sulphide (D 1·225), the remaining procedure being that given for the electrolytic determination of tin in ordinary bronze (*see* p. 232).

2. *Gravimetrically.* The filtered and washed metastannic acid precipitate is dried at 100° and removed as far as possible from the filter to a tared porcelain crucible. The filter-paper is incinerated in a dish, the ash added to the precipitate, the whole moistened with a few drops of nitric acid, the excess of acid evaporated and the residue ignited at first with an ordinary flame and afterwards by means of the blowpipe, and weighed [1]: $SnO_2 \times 0{\cdot}7881 = Sn$.

**2. Determination of the Lead alone or of the Tin alone.**

1. LEAD ALONE. This is of interest in some tin-lead alloys composed mainly of tin, such as solder for culinary utensils and the like.

In a covered electrolytic beaker of 350 c.c. capacity, 1–3 grams of the alloy as filings are treated, according to the amount of alloy taken, with 6–20 c.c. of fuming nitric acid (D 1·5), 3–9 c.c. of water being then allowed to flow slowly down the wall of the beaker. When the attack of the metal is complete, the liquid is boiled for a short time, diluted to about 250 c.c. and thoroughly mixed with 2–3 grams of copper nitrate or with 1–1·5 gram of pure copper dissolved in a little nitric acid, the metastannic acid being allowed to settle and the liquid, *without filtering*, electrolysed to determine the lead: Winkler cathode; matte gauze cylinder anode; $ND_{100}$, 0·3 amp. and voltage, 2–2·2. The cathode should touch the bottom of the beaker, whilst the anode should not reach to within about 1 cm. from the layer of precipitate (for the factor, $Pb : PbO_2$, *see* p. 258). In this way, even the small quantities of lead held by the metastannic acid may be liberated by the current.

2. TIN ALONE. In other types of alloy, consisting essentially of lead (sometimes hard lead) with small quantities of tin (0·5–15%), such as are used for tubes for perfumery, colours, etc., wires for electric valves, etc., it is of interest to determine the tin alone.

From 2 to 3 grams of the sample in filings or clippings are treated with 20–25 c.c. of boiling conc. sulphuric acid and, when the action is at an end, the liquid diluted somewhat. When the liquid is cold, 5–6 grams of tartaric acid are dissolved in it and the whole transferred to a 100 c.c. measuring flask, made up to volume, and filtered through a dry filter. The tin is determined in 50 c.c. of the filtrate in the way given for the determination of tin in hard lead (*see* p. 248).

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The composition of *solder* varies widely with the metals to be soldered and with the resistance to be offered to mechanical action, heat, etc. Solders for coarse work contain about 30% of tin and 70% of lead, whilst those for soft soldering of small articles contain about 70% of tin and 30% of lead; in some cases as much as 90% or more of tin are present. The most readily fusible alloy (183°) contains 37% of lead and 63% of tin.

[1] In this way any antimony present is calculated as tin. For the separation of tin from antimony, *see* White Metals.

## TIN-FOIL

Tin-foil, properly so called, should consist of thin sheets of pure tin and is hence analysed as described for tin. Often, however, it is formed of lead and tin, or of lead, antimony and tin, and in some cases is tinned to obtain the shining white colour of tin. With these last two types of tin-foil, the most important determination is that of the tin, this being effected as for the tin alone in lead-tin alloys (*see* Alloys of Lead and Tin, p. 258). A complete analysis may be carried out by the method indicated for the analysis of lead-tin alloys, when these are the only constituent metals, or by that given for white metal in the case of an alloy of lead, antimony and tin.

If the foil is tinned externally, the coating must be removed in order that the quantity of tin actually present in the alloy may be determined. If the foil is moderately thick, the surface layer may be removed mechanically from the two faces and the quantitative determination made on the sample thus prepared. If, however, the foil is too thin and weak to be scraped, the surface tin is removed by means of sodium hydroxide solution and hydrogen peroxide, which, at the proper concentration, easily attacks and dissolves the layer of tin, whereas the tin in the alloy is acted on either not at all or but slightly. The conditions to be observed are as follows [1]:

From 5 to 6 grams of the foil are freed from grease by treatment with ether, cut into squares of about 1 cm. side and heated in a 200 c.c. flask with 20 c.c. of 10% sodium hydroxide to 40°, 6–8 drops of 30% (100 volume) hydrogen peroxide being then added with continual shaking. The surface tin passes rapidly into solution and as soon as the lead-grey colour assumed by the pieces of metal indicates that this process is complete, the alkaline solution is decanted off and the residue washed repeatedly with water, alcohol and ether successively and dried at 60–70°. The foil being thus freed from the surface tin, the quantitative determination of the components of the alloy is carried out by the methods indicated above.

## WHITE METAL

This includes many types of alloys with a basis of tin-antimony, lead-antimony or lead-tin-antimony, together with small quantities of copper and sometimes zinc and iron (rarely mercury and arsenic), used as antifriction metals, type metal, metal for fittings, etc. The composition, and therefore the analytical methods to be used, vary with the purpose of the metal. Three groups may be distinguished:

(1) *Alloys with a basis of tin* (70–85%) and *antimony* (10–15%), with a little copper (5–10%) and lead (0·5–2%), and perhaps zinc and iron.

(2) *Alloys with a basis of lead* (60–80%), *antimony* (10–15%) and *tin* (10–25%), with a little copper (0·5–1%) and perhaps zinc, iron and arsenic.

(3) *Alloys with a basis of lead* (75–90%) and *antimony* (10–25%), with a small quantity of tin and copper (0·5–2%).

[1] Belasio: "Determination of Tin in Foil of Lead, Tin and Antimony Tinned Externally" (*Ann. Labor. Chim. Gabelle*, VI, p. 231).

For each group the method of analysis will be described later, but since for certain purposes only the content of copper or tin is of interest, a general method is given which permits of the direct and moderately rapid determination of each of these elements.

**1. Direct Determination of the Copper.**[1]—In a 200 c.c. measuring flask, 5 grams of the alloy are heated gently with 20–25 c.c. of nitric acid (D 1·2); when the action is complete, the nitrous vapours are eliminated by short boiling and the liquid cooled, treated with 3 c.c. of conc. sulphuric acid, again cooled, diluted somewhat, rendered alkaline with ammonia, treated with 15–20 c.c. of 10% sodium phosphate solution and made up to volume and mixed. After standing, the liquid is filtered through a dry filter and 100 c.c. of the filtrate neutralised with nitric acid, treated with 6 c.c. of conc. nitric acid and 20 c.c. of 10% sulphuric acid, and electrolysed: Winkler cathode; spiral Winkler anode; $ND_{100} = 0{\cdot}2$ amp.; voltage = 1·8–2·2; and duration, 10–12 hours.

When the copper is completely deposited, the electrolytic beaker is replaced by another small beaker full of distilled water acidified slightly with sulphuric acid, the cathode being detached after some time, washed with water, alcohol and ether, dried at 70° and weighed. (Weight of copper found) × 40 = percentage of copper in the sample.

If the alloy contains arsenic, the copper deposited may have a brown colour. In this case the deposit is dissolved in 5–6 c.c. of nitric acid and the liquid diluted and again electrolysed.

**2. Direct Determination of the Tin.**—According to the supposed tin content, 1–3 grams of the alloy in fine filings are treated with 15–20 c.c. of concentrated, boiling sulphuric acid, the subsequent procedure being that indicated for the direct determination of tin in hard lead (*see* p. 247).

## 1. Alloys with a Tin-Antimony Basis

These alloys usually contain 70–85% Sn, 10–15% Sb, 5–10% Cu, 0·5–2% Pb, with possibly zinc and iron. Their complete analysis is carried out as follows:

*A.* **Electrolytically.**[2]—In a conical flask covered with a small funnel, 0·5–1 gram of the alloy in turnings or filings is treated with the least possible quantity of aqua regia (10–15 c.c.). When the action is over, 10–15 c.c. of water containing in solution 2–3 grams of tartaric acid are added and the liquid made slightly alkaline with concentrated caustic soda solution and treated with a further quantity of 2 grams of sodium hydroxide and 10–15 c.c. of sodium sulphide solution (D 1·225). The liquid is heated on a water-bath with frequent shaking and after about 15 minutes—when the sulphides insoluble in sodium sulphide have settled—filtered by decantation through a filter moistened with sodium sulphide into a tared Classen dish. The residue is washed by decantation five or six times with tepid sodium sulphide (70–80 c.c. in all) and then once with a very little hot water containing a few drops of sodium sulphide. The filtrate contains

[1] Belasio: *Ann. Labor. Chim. Gabelle*, VI, p. 284.
[2] Belasio: *Ann. Labor. Chim. Gabelle*, VI, p. 217.

all the antimony and tin (*see* 1, 2) and the residue insoluble in sodium sulphide the copper and lead and also any zinc and iron present (*see* 3, 4).

1. DETERMINATION OF THE ANTIMONY. The filtrate is treated with 7–8 grams of pure potassium cyanide (precipitated by alcohol) and electrolysed at the ordinary temperature to determine the antimony: Classen capsule cathode; disc or spiral anode; $ND_{100} = 0{\cdot}15–0{\cdot}17$ amp.; voltage = 1–1·2; and duration = 15–17 hours.

When the whole of the antimony is deposited, the electrolyte is poured into a ½-litre flask and the capsule and disc (or spiral) washed with a little water which is also poured into the flask. The capsule is then thoroughly washed with water, alcohol and ether, dried at 70° and weighed.

2. DETERMINATION OF THE TIN. The alkaline liquid freed from antimony is acidified faintly with dilute sulphuric acid (1 vol. acid, 2 vols. water), the flask being kept under a hood, covered with a funnel and shaken. The liquid is then boiled for some time to expel the bulk of the hydrogen sulphide and cyanogen compounds, left on a boiling water-bath for about 15 minutes and filtered through a filter-paper moistened with ammonium sulphate solution, the precipitate being washed with a little hot water saturated with hydrogen sulphide.

The filter and precipitate are then heated to boiling in a small covered beaker with 20 c.c. of conc. hydrochloric acid and 15–20 c.c. of 10% ammonium chloride solution, a few crystals of potassium chlorate being subsequently added to complete the action. The liquid is then diluted with 15–20 c.c. of boiling water, shaken and filtered into a ½-litre flask, washing with hot water acidified with hydrochloric acid. The filtrate is rendered slightly alkaline with ammonia, treated with 5 grams of oxalic acid and heated a little, 5 grams of ammonium oxalate being added to the clear solution, which is then made up to 150–200 c.c. and subjected to a moderate current of hydrogen sulphide while gently boiling. Under these conditions the traces of copper dissolved in the sodium sulphide and also any arsenic present are precipitated. After about an hour the liquid is allowed to cool somewhat in the stream of hydrogen sulphide and is then filtered into a ½-litre beaker and the filter washed with a hot 1% oxalic acid solution saturated with hydrogen sulphide. The filtrate is boiled with 25 c.c. of conc. hydrochloric acid and 12–14 grams of ammonium oxalate for about 15 minutes to expel the hydrogen sulphide, allowed to cool a little, treated with 3–4 drops of 30% hydrogen peroxide, boiled again, cooled to about 50° and, without removal of any suspended sulphur, electrolysed to determine the tin (*see* Electrolytic Determination of Tin in Ordinary Bronzes).

3. DETERMINATION OF THE COPPER AND LEAD. The filter and hydrogen sulphide precipitate (*see* 2) are incinerated in a small dish and then ignited, the residue being dissolved in 2–3 c.c. of nitric acid.

The sulphides remaining undissolved in the sodium sulphide (*see A*) are dissolved in 10–15 c.c. of boiling nitric acid (D 1·2), filtered by decantation, the residue being treated again twice with nitric acid and the united nitric acid solutions (including that from the hydrogen sulphide precipitate) used for determining the lead and copper as well as any zinc and iron present.

If the copper preponderates over the lead, as is usual with alloys of this

group—which scarcely contain impurities of lead—the copper and lead are at once determined simultaneously (*see* Electrolytic Determination of Copper and Lead in Ordinary Brass). If, however, the lead is in the preponderance, it is separated and determined as sulphate, the copper being then determined in the filtrate (*see* Determination of Lead and Copper in Complex Brasses).

4. DETERMINATION OF THE IRON AND ZINC. The liquid from which the lead and copper have been separated is used for the determination of the iron and zinc as in ordinary brasses.

5. DETERMINATION OF THE ARSENIC. *See* Determination of Arsenic in Tin.

*B.* **Gravimetrically.**—2 grams of the sample are acted on with the least possible quantity of aqua regia at a gentle heat on a water-bath. When the action is complete, the liquid is diluted with 10–15 c.c. of water containing 2–3 grams of tartaric acid in solution, then rendered faintly alkaline with sodium hydroxide solution and treated with *colourless* sodium sulphide in very slight excess. The liquid is heated on a water-bath with occasional shaking until the precipitate has settled and is then filtered by decantation, hot water containing a little sodium sulphide being used for washing. The filtrate, containing tin and antimony, is analysed according to 1 and the precipitate, containing lead, copper, etc., according to 2.

1. DETERMINATION OF THE TIN AND ANTIMONY. The filtrate is made up to 1 litre and 200 c.c. treated in a ½-litre flask with 6 grams of potassium hydroxide, 3 grams of tartaric acid and slowly and, if necessary, with cooling, sufficient 30% hydrogen peroxide to decolorise the solution, that is, to transform the sodium sulphide completely into sulphate. The liquid is boiled for some time to expel excess of hydrogen peroxide, allowed to cool, neutralised with saturated oxalic acid solution and treated with 5 grams of solid oxalic acid, diluted to about 250 c.c. and subjected at the boiling point to a moderate current of hydrogen sulphide for about an hour. The solution is then allowed to cool somewhat in the stream of hydrogen sulphide and the antimony sulphide filtered off and washed with 1% oxalic acid solution saturated with hydrogen sulphide.

Since this antimony sulphide may contain small quantities of tin, it is dissolved in a mixture of 10–15 c.c. of conc. hydrochloric acid and 10–15 c.c. of 10% ammonium chloride solution, a few crystals of potassium chlorate being added when the mixture begins to boil. After dilution with water, the liquid is filtered, made slightly alkaline with ammonia, treated with 5 grams of oxalic acid, diluted to 150 c.c. and the boiling liquid again treated with hydrogen sulphide.

(a) *Determination of the tin.* The two filtrates are united, rendered distinctly alkaline with ammonia, acidified with acetic acid, and a current of hydrogen sulphide passed through the solution for about three hours. After a rest of about 30 minutes on a water-bath to facilitate the separation of the precipitate, the latter is filtered off and washed with hydrogen sulphide solution containing a little ammonium sulphate. The tin sulphide thus obtained is dried at 120°, transformed by ignition into the oxide and the latter weighed: $SnO_2 \times 0{\cdot}7881 = Sn$.

(b) *Determination of the antimony.* The antimony sulphide on the filter (*see* 1) is dissolved in a little yellow ammonium sulphide, the solution evaporated in a tared porcelain crucible, the residue treated carefully, to avoid spurting, with nitric acid and the liquid evaporated to dryness. The treatment with nitric acid is repeated twice to ensure the complete oxidation of the sulphur, the residue being ignited and weighed: $Sb_2O_4 \times 0{\cdot}7898 = Sb$.

2. DETERMINATION OF THE LEAD, COPPER, IRON AND ZINC. The sulphides remaining undissolved in sodium sulphide are dissolved in nitric acid (D 1·2), the filtered solution treated with a little sulphuric acid and evaporated until white fumes appear, the subsequent procedure being as indicated for the gravimetric determination of lead, copper, iron and zinc in ordinary brass.

## 2. Alloys with a Lead-Antimony-Tin Basis

These alloys usually contain 60–80% Pb, 10–15% Sb, 10–25% Sn, a little copper and possibly zinc, iron, arsenic. The complete analysis is carried out as follows:

*A.* **Electrolytically.**—1 gram of the sample in fine filings is treated with 20 c.c. of conc. hydrochloric acid and 2–3 c.c. of conc. nitric acid and left overnight in order that the action may proceed slowly but completely.

1. DETERMINATION OF THE LEAD. The acid solution is treated with 10 vols. of absolute alcohol (220–230 c.c.), cooled and after a suitable rest (3–4 hours)—when the bulk of the lead chloride has separated (only a few milligrams, to be estimated later, remain in solution)—filtered through a tared Gooch crucible, washed with alcohol to a neutral reaction, dried at 100° and weighed: $PbCl_2 \times 0{\cdot}7447 = Pb$.

2. DETERMINATION OF THE TIN, ANTIMONY, COPPER, IRON AND ZINC. The alcoholic solution, freed from lead chloride, is evaporated with 2–3 grams of tartaric acid until the alcohol is completely expelled, then made slightly alkaline with concentrated sodium hydroxide solution and treated with 2 grams of sodium hydroxide and 15–20 c.c. of sodium sulphide solution (D = 1·225). After being heated for about 15 minutes on a water-bath, the liquid is filtered into a Classen capsule, the precipitate being washed five or six times with sodium sulphide solution (60–70 c.c. in all) and then with hot water containing a few drops of sodium sulphide. The filtrate contains the tin and antimony and the insoluble residue the copper, traces of lead dissolved as chloride, and any iron and zinc present.

For the electrolytic determination of these elements, the method previously described (*see* 1, *A*, p. 261) [1] is followed.

*B.* **Gravimetrically.**

1. DETERMINATION OF THE LEAD. 1 gram of the sample is attacked with aqua regia and the lead separated as chloride under the conditions described above (*see A*).

[1] If the copper is present in very small amount, it is more convenient to make the direct determination (*see* p. 261) and in such case, when the lead in solution as *chloride is to be* determined, it is advisable to add a little copper nitrate to the electrolyte.

2. DETERMINATION OF THE TIN, ANTIMONY, COPPER, IRON AND ZINC. The alcoholic solution is evaporated with 2–3 grams of tartaric acid until the alcohol is completely expelled, the residue being taken up in water and the liquid made faintly alkaline with concentrated sodium hydroxide solution and treated with colourless sodium sulphide solution in very slight excess. The liquid is heated on the water-bath and filtered, the subsequent procedure being that for the gravimetric analysis of alloys with a tin-antimony basis containing a little copper (*see* p. 263).

## 3. Alloys with a Lead-Antimony Basis

These alloys usually contain 75–90% Pb, 10–25% Sb, and small quantities of tin and copper (0·5–2%). Their complete analysis is carried out by the methods given for hard lead.

***

White metals vary in composition according to their uses, the analytical results for some of the commoner types being as follows:

TABLE XXXIII

**Composition of White Metal**

| Type. | Sn | Pb | Sb | Cu | Fe | Zn |
|---|---|---|---|---|---|---|
| *Antifriction metals:* | | | | | | |
| Adopted by the Italian Railways | 83 | — | 11 | 6 | — | — |
| ,, ,, French ,, | 83·33 | — | 11·11 | 5·55 | — | — |
| ,, ,, Russian ,, | 90 | — | 8 | 2 | — | — |
| | 78·5 | — | 11·5 | 10 | — | — |
| ,, ,, German ,, | 83 | — | 11 | 6 | — | — |
| ,, ,, Austrian ,, | 82 | — | 12 | 6 | — | — |
| English white bearing metal | 76·7 | — | 15·5 | 7·8 | — | — |
| Britannia metal | 90–92 | — | 8–9 | up to 3 | — | — |
| *Antifriction and fittings metals:* | | | | | | |
| Adopted by the Italian Railways | 14 | 76 | 10 | — | — | — |
| ,, ,, French Northern Railway | 12 | 73 | 15 | — | — | — |
| ,, ,, French Eastern Railway | 12 | 80 | 8 | — | — | — |
| ,, by certain German Railways | 42 | 42 | 16 | — | — | — |
| Graphite metal | 15 | 68 | 17 | — | — | — |
| English bearing metal | 53 | 33 | 10·6 | 2·4 | — | 1 |
| American antifriction metal | — | 78·4 | 19·6 | — | 0·7 | 1 |
| Type metal | 15–25 | 50–55 | 25–30 | trace | — | — |
| ,, ,, | 5 | 80 | 15 | trace | — | — |
| Magnolia metal | — | 83·5 | 16·4 | — | — | — |
| ,, ,, | — | 78 | 21 | — | — | — |

## NICKEL AND ITS ALLOYS

Nickel is largely used for nickel plating and for coins of low value, and also occurs in many alloys.

Descriptions will be given here of the tests to be made on commercial nickel and of the analysis of german silver and the like, which are the most important nickel alloys. For the analysis of bronzes containing nickel, *see* Nickel-bronzes.

### NICKEL

The more common determinations involved in the analysis of commercial nickel are those of copper, cobalt, iron, manganese, carbon, sulphur, arsenic and silicon.

10 grams of the sample are dissolved in nitric acid and evaporated in presence of sulphuric acid until dense white fumes appear. When cold the residue is treated with water acidified with sulphuric acid, heated to boiling, filtered and washed with boiling water acidified with sulphuric acid. The residue on the filter is treated according to 1 and the filtrate as described in 2, 3 and 4.

**1. Determination of the Silicon.**—The insoluble residue, consisting of silica and possibly metastannic acid, graphitic carbon, etc., is dried, ignited in a platinum crucible, weighed, treated with hydrofluoric acid and a few drops of sulphuric acid, heated to expel excess of acid, again ignited, cooled and weighed. The loss in weight gives the silica and therefore the silicon (*see* Determination of the Silicon in Iron).

**2. Determination of the Copper.**—The copper is precipitated in the filtrate by means of hydrogen sulphide and is then determined either as oxide or electrolytically by dissolving the sulphide in nitric acid and electrolysing the solution.

**3. Determination of the Nickel and Cobalt.**—(a) *Determination of the nickel.* The filtrate from the copper sulphide is made up to volume in a 500 c.c. measuring flask, and 100 c.c. (corresponding with 2 grams of the sample) evaporated to dryness. The residue is taken up in ammonia and the volume then made up to 100 c.c. with ammonia (D 0·91), 5 grams of ammonium sulphate being dissolved in the liquid and the latter electrolysed to determine the nickel and cobalt together: Winkler cathode; spiral Winkler anode; $ND_{100} = 0{\cdot}7–1$ amp.; temperature, ordinary, and duration, 15–17 hours.

The cathode is subsequently withdrawn, washed, dried and weighed, the increase in weight representing nickel and cobalt; the latter is then determined separately as follows:

(b) *Determination of the cobalt.*[1]—The nickel and cobalt deposited on the electrode are dissolved in nitric acid, the solution evaporated to dryness, the residue taken up in a little water and evaporated with 20 grams of pure ammonium thiocyanate until the salts begin to crystallise out, and the whole washed by means of a little water into a Rothe extraction apparatus.

[1] *Ber. deutsch. Chem. Gesell.*, 1901, XXXIV, p. 2050.

It is here shaken with 50 c.c. of a mixture of 25 vols. of ether with 1 vol. of amyl alcohol, and the ethereal layer—which, in presence of cobalt, is blue—separated, a few drops of concentrated thiocyanate solution being used for washing. The extraction with the ether-amyl alcohol mixture is repeated three or four times, until, indeed, it remains perfectly colourless after the shaking. The various solutions containing the cobalt are then shaken together in the same Rothe apparatus with dilute sulphuric acid, into which the cobalt passes. The aqueous layer is separated—washing with a little dilute sulphuric acid—and evaporated to dryness, the residue being taken up in a little water, the solution made faintly ammoniacal and any traces of nickel present with the cobalt precipitated with alcoholic dimethylglyoxime solution. The precipitate is filtered off, the filtrate evaporated in a small flask with nitric and sulphuric acids to destroy organic matter, and the residual liquid placed in a tared crucible, where the excess of the acids is expelled and the remaining cobalt sulphate then weighed: $CoSO_4 \times 0{\cdot}3804 = Co$.

**4. Determination of the Iron and Manganese.**—The 400 c.c. of solution left (8 grams of the sample)—quite free from hydrogen sulphide—are diluted to about 1·5 litre, treated with hydrogen peroxide and made alkaline with ammonia, heated and then left at rest for a short time on a water-bath, the supernatant liquid being subsequently siphoned off and the precipitated iron and manganese oxides collected on a filter. The precipitate is dissolved in a little hydrochloric acid and the precipitation with hydrogen peroxide and ammonia repeated, the precipitate being filtered off after a short rest on the water-bath, washed with slightly ammoniacal water, dried, ignited and weighed.

This gives the ferric and manganese oxides together. The iron alone is then determined either by titration or by separating it as basic acetate.

**5. Determination of the Carbon.**—3 grams of the sample are dissolved on the water-bath in concentrated copper-potassium chloride solution, the carbonaceous residue being collected on an asbestos filter, washed, dried and burnt in a current of oxygen (*see* Determination of Carbon in Iron, p. 168).

**6. Determination of the Sulphur.**—10 grams of the sample are dissolved in nitric acids, evaporated several times with hydrochloric acid and finally taken up in water and hydrochloric acid and filtered. In the filtrate the sulphuric acid formed by oxidation of the sulphur is precipitated with barium chloride solution.

**7. Determination of the Arsenic.**—From 10 to 20 grams of the sample are dissolved in nitric acid, the solution evaporated with sulphuric acid until the nitric acid is completely expelled, the residue dissolved in water, treated with 5–10 grams of ferrous sulphate and excess of hydrochloric acid and the arsenic determined by distillation (*see* Determination of Arsenic in Iron).

***

Commercial nickel is more or less pure according to the processes used to obtain it. Of the impurities which it may contain (Cu, Co, Fe, Mn, Sn, Pb, Sb, Ca, Al, C, S, Si, $SiO_2$, P, As), the most injurious, especially if the metal is to

be used for preparing alloys, are sulphur, arsenic and iron. Cobalt, which is always present in commercial nickel to the extent of 1–2%, copper, which does not exceed 1%, and the other elements mentioned above, provided these are present only in small proportions, have no deleterious effect on the technical properties of the metal.

The following table gives the properties of samples of nickel of different sources (Lunge, Hollard) :

TABLE XXXIV

**Results of Analyses of Nickel**

| Origin. | Ni | Co | Cu | Mn | Fe | Sb | As | Pb | S | C | Si | $SiO_2$ | $Al_2O_3$ | CaO and Alkalies | P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| German Cubes I | 97·08 | 0·89 | 0·15 | — | 1·22 | — | — | — | trace | 0·02 | — | 0·35 | 0·12 | trace | — |
| German Cubes II | 98·21 | 1·19 | 0·07 | — | 0·25 | — | — | — | trace | trace | — | 0·24 | trace | trace | — |
| Granules from "Königswarter and Ebell" | 98·58 | 0·75 | 0·10 | — | 0·24 | — | — | — | trace | trace | 0·26 | — | trace | trace | — |
| English cubes | 96·86 | 1·26 | 0·06 | — | 1·05 | — | — | 0·40 | trace | 0·09 | — | 0·10 | trace | trace | — |
| "Landore" cylinders | 97·48 | 1·05 | 0·06 | — | 0·79 | — | — | — | trace | trace | — | 0·38 | 0·22 | trace | — |
| Unknown origin I | 95·17 | 1·71 | 1·13 | 0·91 | 0·58 | — | trace | — | trace | 0·22 | — | 0·16 | 0·03 | trace | — |
| Unknown origin II | 92·58 | 0·94 | 3·77 | 1·49 | 0·31 | 0·04 | trace | — | trace | 0·18 | — | 0·39 | 0·14 | trace | 0·05 |
| French coinage [1] | 97·75 | 1·587 | 0·102 | — | 0·259 | — | — | — | 0·039 | — | — | 0·254 | — | — | — |
| Electrolytic nickel | 99·22 | 0·71 | 0·01 | 0·046 | — | — | 0·006 | — | — | — | — | — | — | — | — |

## GERMAN SILVER

## (Argentan, Packfong, Alfénide)

Owing to their colour and stability, these alloys are used for domestic articles, for ornaments in place of silver, for coinage, etc. They all consist essentially of copper, nickel and zinc, sometimes with small quantities of lead and iron and, in rare cases, tin and manganese. Other alloys of similar appearance, used for coating rifle bullets or for coinage, consist of 70–80% Cu, 20–30% Ni, and small proportions of lead, iron, zinc, etc.

The analysis of german silver and of copper-nickel alloys in general is carried out as follows :

### *A.* Electrolytically [2]

In a small covered beaker, 0·5 gram of the alloy is gently heated on a water-bath with 15 c.c. of nitric acid (D 1·2), the solution being subsequently diluted with 20–30 c.c. of water. Turbidity indicates tin, which is determined as in 1 ; a perfectly clear liquid is, however, used at once for the determination of copper and lead (*see* 2).

**1. Determination of the Tin.**—The liquid is evaporated to dryness, the residue taken up in a little water and a few drops of nitric acid and the liquid heated for some time and filtered through a compact filter-paper into a 300 c.c. beaker. The precipitate is washed first with hot water slightly acidified with nitric acid and then with water alone, dried, ignited in a porcelain crucible and weighed : $SnO_2 \times 0{\cdot}7881 = Sn$.

[1] The nickel supplied to the Italian mint for 0·2 lira pieces must contain 97·50% Ni and not more than 1·5% Co, 0·8% Fe or 0·5% of other impurities.

[2] Belasio : *Annali Soc. Chim. di Milano*, 1908, XIV, p. 244.

**2. Determination of the Copper and Lead.**—In absence of tin, the nitric acid solution is at once diluted to about 150 c.c. and electrolysed for the simultaneous determination of the copper and lead (*see* Electrolytic Determination of the Copper and Lead in Ordinary Brasses, p. 224).

If, however, the alloy contains tin and the solution is evaporated to dryness to separate the metastannic acid, the filtrate is treated with 15 c.c. of nitric acid (D 1·2), diluted to 150 c.c. and electrolysed.

**3. Determination of the Iron.**—The liquid from which the copper and lead have been separated, together with the wash water from the first beaker, is evaporated until white fumes of sulphuric acid appear, in order to transform the nickel and zinc nitrates into sulphates; the 10% sulphuric acid (20 c.c.) added to the electrolyte is sufficient for this purpose. When cold, the residue is taken up with water acidified with sulphuric acid and heated on the water-bath, the clear solution being treated with a few drops of hydrogen peroxide and made alkaline with ammonia. After a short rest on the water-bath, the precipitate is filtered off, dried, ignited and weighed: $Fe_2O_3 \times 0{\cdot}6994 = Fe$.

**4. Determination of the Nickel.**—The filtrate from the ferric hydroxide is made up to about 150 c.c. and then mixed with 30 c.c. of concentrated ammonia and 0·1 gram of hydroxylamine sulphate, the electrodes being arranged but the circuit not closed. A thermometer is fitted and the beaker covered with the two halves of a clock-glass having gaps for the stems of the electrodes and for the thermometer and heated to 90°. One or two drops of fresh concentrated sodium sulphite solution are then added and the electrolysis immediately started, the temperature being kept at about 90° and occasional small quantities of ammonia (1 vol. conc. ammonia to 1 vol. water) added from a wash-bottle to replace that lost owing to the heating: Winkler cathode; spiral Winkler anode, $ND_{100}$ = 0·1 ampere; voltage = 2; temperature = 90°; duration (0·1 gram Ni) about 2 hours.

When the liquid changes from blue to colourless, a drop of it is withdrawn and treated with alcoholic dimethylglyoxime solution to ascertain if the nickel is completely deposited. When this is the case, the flame is extinguished, the thermometer taken out and washed, the cover removed and the electrolytic beaker replaced by another filled with distilled water. After some time the cathode is detached, washed with water, alcohol and ether, dried at 70° and weighed.[1]

**5. Determination of the Zinc.**—In the liquid from which the nickel has been removed, mixed with the wash water contained in the beaker and concentrated to about 150 c.c., the zinc is determined by one of the methods indicated for the electrolytic determination of zinc in ordinary brasses (*see* p. 224).

## *B.* Gravimetrically

**1. Determination of the Tin, Lead, Copper and Iron.**—*See* Gravimetric Analysis of Ordinary Brasses.

[1] Under these conditions the nickel and any cobalt present are deposited simultaneously. For their separation, *see* Analysis of Commercial Nickel.

**2. Determination of the Nickel.**—The slightly ammoniacal liquid from which the ferric hydroxide has been separated is treated with slight excess (about 50 c.c. of reagent are required per 0·1 gram nickel) of 1% alcoholic solution of dimethylglyoxime. The solution is heated for about 30 minutes on the water-bath and—after the completion of the precipitation has been ascertained by pouring a fresh quantity of the reagent down the sides of the beaker—filtered through a tared Gooch crucible, which is repeatedly washed with hot water, dried at 120° and weighed: (weight of the nickeloxime) × 0·2032 = nickel.

**3. Determination of the Zinc.**—The filtrate from the nickel precipitate is evaporated on a water-bath with nitric and sulphuric acids to eliminate the excess of alcohol and destroy the excess of dimethylglyoxime. The residue is taken up in water, the solution neutralised exactly with ammonia and treated with 8–10 drops of 2N-hydrochloric acid, and the zinc precipitated as in the gravimetric analysis of ordinary brasses.

**4. Determination of the Cobalt.**—The liquid freed from zinc sulphide is evaporated to 50–60 c.c., neutralised with ammonia and treated at 40–50° with a current of hydrogen sulphide. The cobalt is precipitated as sulphide, which is converted into sulphate and the latter weighed.

Some types of argentan contain also silver (3–10% or even more). In this case, the silver is precipitated as chloride before the copper is determined (*see* Determination of Silver in Commercial Copper). The filtrate from the silver chloride is evaporated in presence of nitric acid to expel excess of hydrochloric acid, the residue being dissolved in water and treated subsequently as above.

Further, manganese is sometimes present. In this case, the tin, lead and copper are determined by the methods given for complex brasses. The iron and manganese are then precipitated with hydrogen peroxide and ammonia, the filtrate being employed for the determination of the nickel and zinc as already described. The iron and manganese precipitated with hydrogen peroxide and ammonia may be separated and determined electrolytically or volumetrically (*see* Complex Brasses); or the ferric and manganese oxides may be weighed together, then dissolved in hydrochloric acid, and the iron separated as basic acetate.

***

As is seen from the following table (Lunge), alloys of copper, nickel and zinc vary in composition according to their origin, purpose, etc.

TABLE XXXV

**Compositions of Argentans**

| | | Cu | Ni + Co | Zn | Mn | Fe | Pb |
|---|---|---|---|---|---|---|---|
| Argentan from Krupps | I | 58·02 | 24·91 | 16·68 | — | 0·25 | 0·11 |
| | II | 60·01 | 22·69 | 16·62 | — | 0·48 | 0·16 |
| Argentan of quality | I | 61·60 | 17·00 | 20·94 | 0·18 | 0·10 | 0·20 |
| | II | 65·78 | 11·43 | 22·19 | — | 0·26 | 0·24 |
| | III | 62·09 | 7·47 | 29·61 | — | 0·25 | 0·53 |
| | IV | 70·94 | 4·99 | 23·63 | — | 0·21 | 0·24 |

Qualities II, III and IV are used especially for sham silver ware.

## IMITATION PLATE

Imitation plate for table ware, trays, etc., consists of argentan with a low proportion of nickel (7-10%) heavily silvered galvanically (it contains 2-3% Ag). Besides the trade-mark, it often exhibits—particularly with forks, spoons, etc.—a number indicating the quantity of silver deposited per dozen pieces. The alloy is analysed like argentan. Usually, however, it suffices to determine only the layer of silver and this may be effected as follows :

**Determination of the Silver.**—1. After being well cleaned and freed from grease, the object is suspended by a platinum wire in a 2-3% potassium cyanide solution in a tall, narrow cylinder and is connected with the positive pole of a current source. A thin, clean copper sheet in communication with the negative pole, is also suspended in the liquid but not in contact with the object. The current (0·1–0·2 ampere) dissolves the silver from the article and deposits it on the copper. When the de-silvering is complete, both the object and the silvered copper are removed and washed, the latter being dissolved in nitric acid, the solution diluted and the silver precipitated by a slight excess of hydrochloric acid ; the silver chloride is collected in a Gooch crucible, washed, dried and weighed.

The hydrocyanic solution is acidified with dilute hydrochloric acid (*under a hood*), the liquid evaporated until cyanogen compounds are completely eliminated, and the precipitated silver chloride weighed. From the sum of the two quantities of silver chloride the amount of silver on the object is calculated.

2. The article, or part of it, is freed from grease, weighed, and gently heated with a mixture of 9 vols. of conc. sulphuric acid and 1 vol. of conc. nitric acid. By this means all the surface silver is rapidly dissolved, whilst the metal beneath is not at all or but little attacked. When the de-silvering is complete, the object is withdrawn, washed rapidly and thoroughly with water,[1] dried and weighed. The loss in weight gives the silver plating.

For a more rigorous determination the silver dissolved may be estimated by diluting with water the nitric-sulphuric solution, together with the washing water, and determining the silver either volumetrically by Volhard's method or gravimetrically as chloride.

## ALUMINIUM AND ITS ALLOYS

Owing to its lightness and stability, aluminium is now used for making many diverse objects in common use and for naval and flying construction. Further, aluminium forms a constituent of numerous alloys, many of which are mechanically superior to pure aluminium. Among these are : *Light aluminium-bronze* (Al with 3–8% Cu) ; *Magnalium* (Al with 3–15% Mg) ; *Barbouze's alloy* (Al with 10% Sn) ; *Ziskon* (Al with varying proportions of zinc) ; *aluminium-nickel* (Al with 1–3% Ni) ; *aluminium-manganese*

[1] Thorough washing is effected by taking the object quickly from the acid mixture and immersing it in a fairly large vessel full of water.

(Al with 2–3% Mn); *Duralumin* (Al with 3·5–5·5% Cu, 0·5–0·8% Mn, 0·5% Mg); *Zisium* (Al with varying quantities of Cu, Sn, Zn); *Alluman* (Al with 10–20% Sn, 4–6% Cu). There are also many other alloys of aluminium, nickel and iron; aluminium, copper, lead, nickel and iron, etc.

For commercial aluminium and its more important light alloys, a general method of analysis will be indicated, whilst for light aluminium-bronze and for magnalium, which could also be analysed by the general method, special and quicker methods are given.

For aluminium-copper alloys in which the copper predominates (heavy aluminium-bronzes, aluminium-brasses, etc.), reference should be made to copper and its alloys and for iron-aluminium alloys (ferro-aluminium) to ferro-metallic alloys.

## ALUMINIUM

The elements usually present as impurities in commercial aluminium are copper, lead, iron, zinc, carbon, silicon and sodium. To form the so-called *light alloys*, the aluminium may be associated with tin, copper, zinc, nickel, cobalt, manganese, lead, magnesium, etc.

Thus, the analysis of commercial aluminium or of its lighter alloys includes [1]:

**1. Determination of the Copper, Lead, Iron, Zinc, Manganese and Cobalt.**—*A.* IN ABSENCE OF NICKEL. From 2 to 4 grams of the sample —according as the extraneous metals are present in larger or smaller proportion—in minute fragments are treated in a flask (about ½-litre) with five times their weight of tartaric acid and a little water. The flask is covered with a small funnel and a small quantity of hydrochloric acid diluted with an equal volume of water added drop by drop. The action is started by gentle heating and sometimes proceeds so vigorously as to require cooling. When the evolution of hydrogen begins to slacken, a fresh quantity of hydrochloric acid of the same concentration is added and the liquid heated on the water-bath until the action is complete, care being taken to use the least possible amount of acid. The heating is then continued for some time, with addition of 2–3 c.c. of conc. nitric acid.

The solution, which is usually turbid owing to the presence of carbon and silica, is treated with small quantities of 50% sodium hydroxide solution until the voluminous aluminium hydroxide precipitate at first formed redissolves in the excess of the reagent. Hydrogen sulphide is then passed through until the supernatant liquid becomes faintly yellow and the solution boiled for some minutes to facilitate separation of the sulphides, left for a time on the water-bath and filtered into a 300 or 500 c.c. measuring flask, the precipitate being washed with hot water containing a few drops of sodium sulphide. The copper, lead, iron, zinc, manganese and cobalt remain on the filter, while the aluminium passes into solution, together with any tin present as sulphostannate.

The sulphides on the filter are dissolved in nitric acid (D 1·2) and the

[1] Belasio: *Annali di Chim. Appl.*, 1914, I, p. 101; *Ann. Labor. Chim. Gabelle*, VII, p. 171.

metals determined as in the case of ordinary brasses when manganese is absent, or like complex brasses when manganese is present.[1]

*B.* IN PRESENCE OF NICKEL. In this case, the preliminary removal of the nickel as nickeloxime is necessary. When the metal is attacked as described above, the liquid is filtered to remove the suspended carbon and silica, these being washed and the filtrate treated with ammonia until the copious precipitate first forming redissolves. The last clots of precipitate are dissolved by heating on a water-bath and the clear liquid treated with 1% alcoholic dimethylglyoxime solution in slight excess. After a short stand on a water-bath the precipitate is collected in a Gooch crucible, washed firstly with hot water containing a little ammonia and ammonium tartrate and then with hot water alone until the filtrate is neutral, dried at 120° and weighed: nickeloxime × 0·2032 = nickel.

The filtrate is heated on a water-bath to expel the alcohol and then treated with just sufficient hydrogen sulphide to precipitate the metals in solution, the subsequent procedure being as in *A* (above).

**2. Determination of the Tin.**—The sodium or ammonium sulphide solution in the 300 or 500 c.c. flask is made up to volume and an aliquot part (100 or 150 c.c.) treated, in a ½-litre flask covered with a small funnel, with small quantities of hydrochloric acid and with shaking until the reaction is acid. A further quantity of 25–30 c.c. of conc. hydrochloric acid is added and the liquid boiled, if necessary with addition of a few crystals of potassium chlorate, until the tin sulphide at first separating redissolves in the excess of hydrochloric acid.

The solution is then treated with 25–30 grams of ammonium oxalate and electrolysed at 50–60° to determine the tin (*see* Electrolytic Determination of Tin in Ordinary Bronzes).

**3. Determination of the Carbon.**—This is carried out directly on a portion of the sample by either the Corleis method or the copper chloride method (*see* Determination of Total Carbon in Iron).

**4. Determination of the Silicon.**[2]—1 gram of the aluminium in small fragments is dissolved in 300 c.c. of a mixture of 100 c.c. of nitric acid (D 1·42), 300 c.c. of hydrochloric acid (D 1·2) and 600 c.c. of 25% sulphuric acid. When the action comes to an end, the liquid is heated carefully on a sand-bath until abundant white sulphuric acid fumes appear. When cold the residue is taken up with water acidified with sulphuric acid, heated to dissolve the aluminium sulphate and filtered, the vessel and filter being washed first with water acidified with sulphuric acid and then with water alone.[3] The residue on the filter, consisting of silica, graphitic silicon and a little alumina, is dried, ignited and fused with sodium carbonate, the cold mass being dissolved in water acidified with hydrochloric acid and evaporated to dryness; this treatment with hydrochloric acid is repeated several times and the residue finally heated in an oven at 135° to render the silica completely insoluble (*see* Iron, 2).

[1] Any cobalt present is determined electrolytically under the conditions indicated for the determination of the nickel.

[2] According to I. O. Handy: *Journ. Amer. Chem. Soc.*, *XVIII*, p. 736.

[3] In presence of lead, the washing is carried out first with hydrochloric acid (D 1·2) and then with water, as usual.

The silica, often contaminated with alumina, is filtered off, dried, ignited in a platinum crucible and weighed ; it is then evaporated on a water-bath with a few drops of sulphuric acid and a few c.c. of hydrofluoric acid, heated to redness and weighed. The loss in weight gives the silica : $SiO_2 \times 0{\cdot}4693 = Si$.

**5. Determination of the Sulphur, Arsenic and Phosphorus.**—10 grams of the sample are introduced into a flask fitted with a tapped funnel and a gas-delivery tube connected with absorption bulbs containing bromine water, and very dilute hydrochloric acid slowly run in through the funnel until the metal is completely attacked. The sulphur, phosphorus and arsenic are oxidised by and retained by the bromine water, one-half of which is used for the determination of the sulphuric acid by precipitation with barium chloride. The second half is freed from the excess of bromine and the arsenic precipitated by means of hydrogen sulphide and determined as usual. The filtrate from the arsenic precipitate is freed from excess of hydrogen sulphide and the phosphoric acid then precipitated with ammonium molybdate (*see* Determination of the Phosphorus in Iron).

**6. Determination of the Sodium.**[1]—5 grams of the sample are heated gently with nitric acid (D 1·15), the solution evaporated in a porcelain dish, the residue dried and heated for a long time on a sand-bath, but without melting the sodium nitrate formed. When cold the residue is taken up in boiling water, the solution filtered and the filter washed with boiling water, the filtrate being evaporated to dryness repeatedly with hydrochloric acid to expel the nitric acid and the residue heated to about 300°, allowed to cool, dissolved in water and the chlorine estimated ; the corresponding amount of sodium is then calculated.

Lunge [2] observes that a little sodium aluminate is formed under these conditions and advises the treatment of the aqueous solution with ammonium carbonate to precipitate the aluminium and the determination of the sodium as sulphate in the filtrate.

**7. Determination of the Aluminium.**—0·6 gram of the sample, reduced to fine fragments, is treated in a flask covered with a small funnel, with hydrochloric acid diluted with an equal volume of water. When the action is complete, the solution is evaporated in a platinum dish on a water-bath, this evaporation with dilute hydrochloric acid being repeated several times and the residue finally heated in an oven at 135° to render the silica insoluble. The latter is treated with hot water acidified with hydrochloric acid and filtered into a 250 c.c. beaker, in which it is subjected to a current of hydrogen sulphide. The precipitate is filtered off and both vessel and filter washed with hot water containing hydrogen sulphide, the filtrate being collected in a 300 c.c. flask, boiled to expel hydrogen sulphide, treated with a few drops of conc. nitric acid, heated again to oxidise the iron, cooled and made up to volume. 100 c.c. of the liquid (= 0·2 gram of metal) are treated in a platinum dish or, failing that, a porcelain one, with excess of ammonium chloride and sufficient ammonia to give a

[1] Moissan : *Comptes rendus*, 1895.
[2] *Lunge : Technical Methods of Chemical Analysis* (London, 1911), Vol. II, p. 348.

faintly alkaline reaction. The liquid is boiled for some time and the aluminium and ferric hydroxides filtered off, washed, dried and weighed in the ordinary manner. This amount, less that of the ferric oxide previously found, gives the alumina and hence the aluminium.

If the iron has not been determined previously, it may be estimated in presence of aluminium by means of cupferron.

For this purpose, 100 c.c. of the liquid in the flask are treated in a 250 c.c. beaker, with constant shaking, with 6% aqueous cupferron (ammonium salt of nitrosophenylhydroxylamine) until the precipitation of the iron is complete (0·1 gram Fe requires 0·833 gram of the reagent). The end of the reaction is detected by pouring a little of the reagent down the side of the beaker; when iron is still present, a reddish-brown precipitate is formed whereas in absence of iron a white, crystalline precipitate is formed owing to the slight solubility of the reagent in an acid medium.

After the precipitation of the iron, the liquid is left for 15–20 minutes and then filtered, the precipitate being thoroughly washed first with 2N hydrochloric acid, then with slightly ammoniacal water to eliminate all traces of the reagent, and finally with distilled water. The moist filter and precipitate are then carefully ignited in a porcelain crucible, the weight giving the ferric oxide.[1]

**8. Determination of the Nitrogen.**—From 3 to 4 grams of the sample are dissolved, in a flask fitted with a tapped funnel and a gas delivery tube, with 10% sodium hydroxide solution, the gas generated being collected in dilute hydrochloric acid. At the end of the action, the flask is boiled for a further 15 minutes to displace all the ammonia and the nitrogen in the hydrochloric acid then determined colorimetrically with Nessler solution, comparison being made with a standard ammonium chloride solution.

***

Aluminium of good quality should be white with only a faint blue tint and should be highly ductile and malleable, while its fracture should be finely crystalline, uniform, and free from sponginess or slag. Its specific gravity should be between 2·6 and 2·7 (the value increases with the degree of impurity) and the percentage of aluminium at least 97–98, the total amount of elements commonly accompanying the aluminium (silicon, iron, copper) not exceeding 1·5–2%. According to Moissan, a particularly harmful influence on the strength and durability of the aluminium, especially when this is to come into contact with water, is exercised by sodium, which may be present in the proportion of 0·1–0·4% (Moissan) or, according to some, in even larger amounts (up to 4%). According to Foundry, aluminium also contains 0·04–0·12% of nitrogen. The compositions of various samples are given in the following table (Moissan, Campredon, Lunge):

[1] In the liquid from which the aluminium and iron have been separated, the magnesium is determined in the usual manner.

TABLE XXXVI

**Compositions of Samples of Aluminium**

| Source. | Al | Fe | Cu | Si | Na | C | Pb | P | S |
|---|---|---|---|---|---|---|---|---|---|
| Bussi (Abruzzi) I[1] | 98·86 | 0·77 | — | 0·29 | — | — | — | — | — |
| Bussi (Abruzzi) II[1] | 98·90 | 0·58 | — | 0·50 | — | — | — | — | — |
| Bussi (Abruzzi) III[1] | 99·00 | 0·51 | — | 0·47 | — | — | — | — | — |
| Neuhausen Quality o | 99·90 | 0·04 | — | 0·06 | — | — | — | — | — |
| Neuhausen ,, I | 99·33–99·61 | 0·11–0·34 | — | 0·18–0·58 | — | — | — | — | — |
| Neuhausen ,, II | 92·84–97·65 | 1·37–3·34 | — | 0·94–3·82 | — | — | — | — | — |
| Pittsburg | 98·82 | 0·27 | 0·35 | 0·15 | 0·10 | 0·41 | — | — | — |
| Samples of unknown origin (Campredon) I | 98·4434 | 0·586 | 0·479 | 0·1463 | 0·14 | 0·10 | 0·073 | 1·029 | 0·0027 |
| Samples of unknown origin (Campredon) II | 96·5501 | 1·2320 | 0·939 | 0·1979 | 0·02 | 0·05 | 0·6270 | 0·005 | 0·0038 |

## ALLOYS OF ALUMINIUM AND COPPER[2]

### (Light Aluminium-bronzes)

Light aluminium-bronzes have the specific gravity about 3 and exhibit mechanical properties superior to those of pure aluminium, so that they are used in the construction of parts for automobiles, dirigible balloons, aeroplanes, etc.; those most commonly used contain 3–8% of copper. In practice the most important determination is that of the copper.

**1. Determination of the Copper.**—1 gram of the alloy as filings is acted on in a platinum dish with 5 grams of sodium hydroxide dissolved in 25 c.c. of water. When the action is complete, the insoluble residue, consisting of copper, iron, etc., is collected on a filter, washed well, dissolved in 10–15 c.c. of nitric acid (D 1·2) and the solution, after suitable dilution, electrolysed to determine the copper (*see* Electrolytic Determination of Copper in Ordinary Brasses).

## ALLOYS OF ALUMINIUM AND MAGNESIUM

### (Magnalium)

The most important determination with these alloys is that of the magnesium. 1 gram of the alloy is treated with a mixture of hydrochloric, nitric and sulphuric acids, the liquid being heated until white fumes appear and the silica removed by filtration (*see* Determination of Silicon in Aluminium). In the filtrate the copper, lead, etc., are precipitated with hydrogen sulphide, the precipitate being filtered off, the excess of hydrogen sulphide eliminated, the iron oxidised and the solution neutralised with ammonia, diluted considerably and treated with 30 c.c. of concentrated ammonium acetate solution. The liquid is then boiled to precipitate the

[1] Kindly communicated privately.

[2] For alloys of aluminium and copper (aluminium bronzes) with a preponderance of copper, *see* Special Bronzes.

aluminium and filtered, the filtrate being used for the determination of the magnesium in the ordinary way.

Magnalium usually contains 2% of magnesium but may contain up to 15%. It is lighter, harder and more easily worked than aluminium.

## SILVER AND ITS ALLOYS

The most important of these products are silver in rods, ingots, bar, etc., and its alloys with copper. Their analysis involves in all cases the same procedure.

### SILVER

*See* following article for the determinations to be made.

### SILVER ALLOYS

In commercial silver and its alloys with copper, the most important determination is that of the silver, since these products are valued according to their silver content, referred to 1000 parts. In some cases determination of the small quantity of gold present may be of interest, and in some instances also that of the bismuth. In alloys of silver with gold or with gold and copper, it is usual to determine both the rare metals (*see* Gold and its Alloys). In all cases the sampling is of great importance.

*Sampling.* Silver alloys, especially those with copper, are mostly non-homogeneous, since their solidification is accompanied by the phenomenon of liquation. With silver-copper alloys less than 718 fine (718/1000) the outer parts are richer than the central ones, whereas with those more than 718 fine the reverse is the case. It is, therefore, difficult to obtain a representative sample. The most accurate method is to take the sample from the fused metal in the following way: The liquid mass is stirred by means of a graphited iron spoon, which, when thoroughly heated, is extracted full of metal, two drops of the latter, weighing about 3–4 grams each, being dropped into a cast-iron mould. These drops are then flattened on an anvil, rolled to obtain sheet that can easily be cut with metal shears, and polished with emery cloth.

With ingots, where this method is impracticable, four samples are taken with a drill at different points, namely: two outside on the vertices of a diagonal of the cake of metal and two on two points of the diagonal itself at distances of one-fourth and three-fourths of the length of the diagonal from one of the vertices, the two holes being made one at the top and the other at the bottom of the ingot and the first borings discarded so as to collect portions lying approximately on the diagonal.

With finished products, jewellery, gilt ware, etc., the surface must be filed away, since they are generally whitened and the outer parts may be richer in silver.

In whatever way the sample is taken, the determinations should always be executed in duplicate.

**1. Determination of the Silver.**—The methods most commonly used are: the dry or cupellation method, Volhard's volumetric method with thiocyanate, and Gay-Lussac's sodium chloride method.

(*a*) CUPELLATION METHOD. This method is based on the fact that the noble metals, silver, gold and platinum, are unoxidisable at the highest temperatures, whilst copper and other metals usually alloyed to the precious metals oxidise easily and, if in presence of a certain quantity of lead—which gives a readily fusible oxide—penetrate by imbibition into the cupel. Thus, the noble metals are separated in the form of a drop, which, on cooling, yields a button capable of direct weighing.

*Apparatus and reagents.* (1) Muffle furnace, either coal or gas, the latter more easy to manipulate and regulate. In order to protect the operator from the intense heat of the furnace, the latter is usually placed in an adjacent room close to the dividing wall, a small aperture in which gives access to the orifice of the muffle.

2. Cupels. These are capsules having the form of an inverted, truncated cone and made with bone dust carefully powdered, calcined, washed and pressed in a mould. A good cupel should absorb its own weight of lead.

3. A thermo-electric couple with the corresponding pyrometer voltmeter, to measure the temperature of the muffle. The couple is placed in the muffle so that its extremity is very close to the cupel.

4. Lead free from silver. That obtained by reducing litharge could be used but its price is too high. Lead almost entirely free from silver is, however, sold and is quite suitable; 20 grams of it should be cupelled as a check.

*Preliminary test.* The amount of lead to be used for the cupellation varies with the silver content of the sample, so that it is necessary to make a preliminary test. The external characters and a test on the touchstone are sufficient to a skilled operator. A beginner may make use of a method which is sometimes employed and which consists in cupelling 0·1 gram of the sample with 0·5 gram of lead if the metal is soft and white, with 1 gram of lead if it is hard, or with 1·5 gram, if it appears reddish.

The amounts of lead to be used for different degrees of fineness are as follows:

| Degree of fineness of the alloy. | Amount of lead to cupel 1 gram of the sample |
|---|---|
| 1,000 | 0·3 gram. |
| 950 | 3·0 ,, |
| 900 | 7·0 ,, |
| 800 | 10·0 ,, |
| 700 | 12·0 ,, |
| 600 | 14·0 ,, |
| 600–0 | 16–17 ,, |

*Actual test.* If the fineness is above 800, *two* samples of 1 gram each, and if less than 800, *two* samples of 0·5 gram each are weighed with the

greatest accuracy.[1] These are wrapped in small pieces of white paper or thin lead foil, the weight of which is allowed for in calculating the amount of lead to be used, and placed on a tray consisting of a sheet of copper provided with a handle and stamped into cavities to take the test pieces. Beside each button is placed the necessary quantity of lead.

The cupels are placed in the muffle and close to them the thermo-electric couple,[2] the temperature being then raised to bright redness, that is, to about 950°. When these have assumed the temperature of the muffle (indicated by the absence of a dark zone between the bottom of the cupel and the base of the muffle), the pieces of lead are introduced into the cupels by means of suitable tongs. The lead at first melts and becomes covered with a layer of oxide and after some time *uncovers*, that is, assumes a shiny appearance.

When the lead is uncovered, the test pieces are placed in the cupels with great care to avoid loss by projection, the door of the muffle being left open a little to permit of observation and to give access to the air. The test pieces melt and a shining appearance is resumed. Over the surface of the fused metal, which is at first only slightly convex, luminous points are seen to run and become absorbed by the cupel. As the cupellation proceeds the convexity increases and the drops of fused litharge, of oily appearance, become larger and circulate more rapidly. At this point the temperature should be raised a little by closing the door of the muffle and increasing the draught of the furnace, in order to oxidise the last particles of lead and keep the button of silver fused. As the last portions of lead " pass " from the silver, the molten metal, which is in a state of considerable agitation, exhibits a kind of iridescence, this soon disappearing; the button then appears opaque and still, but suddenly flashes out brightly. This indicates the end of the operation.

The cupels are then gradually brought near to the door of the muffle so that the buttons of silver may cool slowly and rapid release of the occluded oxygen (fused silver absorbs up to 22 volumes of oxygen) not give rise to projection (*spitting or vegetating*) of the metal. After a few minutes the cupels are withdrawn from the muffle and the metallic buttons detached, hammered slightly on both sides, held in tongs and freed with a scratch-brush from the adherent cupel dust and weighed.

The total weight of the two test pieces in milligrams, if these were each of 0·5 gram, or this weight divided by two, if the samples were 1 gram each, gives the fineness of the alloy.

If the cupellation is successful, the silver buttons obtained from the

[1] With samples of silver and gold, to obtain the highest accuracy and to be able to weigh directly, very sensitive balances are employed with an exactly equally divided long beam and with very small movable dish-shaped pans, on which the test pieces are placed directly. The maximum load of such a balance is 2–3 grams.

[2] If no thermo-electric couple and corresponding voltmeter-pyrometer are available, the temperature of the furnace during cupellation may be regulated by observation of the way in which the fumes of litharge are evolved. When the temperature is suitable, the fume rising from the tests should reach only half-way up the muffle and small, lamellar crystals of litharge should be seen on the edge of the cupel. If the temperature is too low, the fume licks round the edges of the cupel, whilst, if too high, it rises rapidly towards the crown of the muffle.

two tests should have shining, hemispherical upper surfaces and opaque, white lower ones, and should differ in weight by a few milligrams at most.

The method of cupellation, largely used for the analysis of argentiferous minerals and for the control of intermediate products in the extraction of silver, as well as for the by-products and for low-grade alloys, is not advisable for analysing ordinary jewellery, coinage, etc., since, however carefully it is carried out, the results obtained are not always concordant and never very exact, being mostly somewhat low. The errors are due principally to volatilisation of the silver and absorption by the cupel. Tables showing the corrections to be applied have been prepared, but the best method of determining such corrections is to carry out a *check* determination, at the same time and under the same conditions, with pure silver and pure copper in approximately the same proportions as in the sample.

As regards the influence of extraneous metals on the results, it should be borne in mind that gold and platinum ***remain with the silver and increase its weight.*** They may be detected by treating the button with nitric acid and examining the black powder remaining undissolved. In low proportions, arsenic, tin, antimony, bismuth, iron, nickel and cobalt do not interfere appreciably with the operation.

(*b*) VOLHARD'S METHOD.[1] This method consists in precipitating the silver in nitric acid solution with standard ammonium thiocyanate solution in presence of ferric sulphate as indicator. As soon as the precipitation of the silver is complete, the thiocyanate reacts with the ferric salt and gives a persistent red coloration, which marks the end of the reaction.

*Reagents.* (1) A solution containing 3·1–3·2 grams of ammonium thiocyanate, free from chlorides, per litre.

(2) Cold saturated ferric ammonium alum solution free from chlorides, and treated with a little nitric acid to destroy the brown colour ; the same amount (2–3 c.c.) is used in each titration.

(3) Pure silver (*fine silver*). This may be obtained in foil from reputable firms.

Where many tests are made the fine silver is prepared in the laboratory from the silver chloride residues from Gay-Lussac's method or from silver chloride precipitated from the silver nitrate solutions obtained in the ***quartation*** of gold (*see* later). Failing these, commercial silver of 999 fineness is dissolved in nitric acid, allowed to stand for some days in the dark, filtered to remove traces of undissolved gold and the silver precipitated with a slight excess of dilute hydrochloric acid.

In whatever way obtained, the silver chloride is washed free from acid, dissolved in ammonia, left for some days and then filtered, the clear solution being made acid with dilute hydrochloric acid to precipitate the silver chloride, which is again washed free from acidity and redissolved in ammonia. After standing for some time, the solution is filtered, treated with sodium hydroxide in the proportion of 750 grams per 1000 grams of the chloride and heated to boiling, 150–200 grams of pure, powdered glucose being added in small amounts and the liquid kept boiling for about 30 minutes. The spongy silver thus obtained is pumped off, thoroughly washed, dried and fused in a refractory crucible with a little nitre and borax.

When cold, the crucible is broken and the metallic button washed with

[1] Also known as the Charpentier-Volhard method.

dilute sulphuric acid, dried, re-melted alone in a smaller crucible and poured into a small ingot-mould heated and greased with tallow or vaseline. The ingot obtained is thoroughly cleaned, washed first with dilute sulphuric acid and then with water and dried. It is then cut into pieces with a chisel, and these rolled into strips easily cut with the metal shears.[1]

*Titration of the thiocyanate solution.* Exactly 0·2 gram of fine silver is heated gently with 5–10 c.c. of nitric acid (D 1·2) in a conical flask covered with a funnel until the metal is dissolved and the red fumes have disappeared. The funnel is removed after *cooling* and washed with distilled water, the solution being treated with 50 c.c. of cold water and 2–3 c.c. of the ferric alum solution, and the thiocyanate solution gradually run in from a burette until the milky liquid assumes a persistent pink tint. It is usual to adjust the strength of the thiocyanate solution so that 0·2 gram of silver requires exactly 50 c.c.

*Procedure in the actual test.* Exactly 0·2 gram of the sample is dissolved in nitric acid[2] as described above and the solution diluted and titrated with the thiocyanate.

The Volhard method is very rapid and applicable to alloys of any degree of fineness but is not so exact as Gay-Lussac's method (*c*). Further, it cannot be used in presence of mercury or palladium, since these metals also react with thiocyanate. Also, with more than 70% of copper, the blue coloration renders the end-point less exact; in this case fine silver may be added so as to diminish the proportion of copper. Nickel and cobalt have a similar effect to copper.

(*c*) GAY-LUSSAC'S METHOD. This was proposed in 1832, when the French Minister of Finance appointed a commission, of which Gay-Lussac was a member and also reporter, to study the causes of error in the determination of silver by the cupellation method.[3]

It consists in adding to a nitric acid solution of the sample sufficient sodium chloride solution to precipitate almost the whole of the silver, and in estimating the small amount of silver remaining in solution from the faint turbidity produced by addition of a fresh quantity of the sodium chloride solution. With a little practice, 1 part in 10,000 may be determined accurately by this method. Since it requires a knowledge of the approximate composition of the sample, a preliminary test by Volhard's method or by cupellation is necessary.

*Apparatus.* 1. Ordinary bottles of about 200 c.c. capacity, fitted with tight-fitting ground stoppers and with a distinctive mark on both bottle and stopper.

2. A 100 c.c. pipette. The pipettes used by assayers are usually without a stem and, to facilitate reading, are fixed in a stand (Fig. 24).

Increased accuracy of measurement is, however, obtained by means of the Stas pipette (Fig. 25), which is a 100 c.c. pipette drawn out to a point

[1] This method for obtaining fine silver is that adopted by the testing laboratory of the Royal Italian Mint at Rome.

[2] No nitrous fumes should be present in the nitric acid used and those formed during the reaction should be completely expelled, since nitrous fumes—and nitric acid itself in the hot—decompose thiocyanates.

[3] Gay-Lussac: *Instruction sur l'essai des matières d'argent par la voie humide*, Paris, Imprimerie royale.

at each end. At the upper end is fixed, by means of a rubber stopper, a glass basin to catch the overflow, while the lower end is connected by a rubber tube and tap with the vessel containing the sodium chloride solution fixed at a convenient height. The pipette is filled by opening the tap and allowing the liquid to flow gently over. When the liquid begins to overflow at the top, the latter is closed by means of the index finger of the left hand, while the tap is shut and the rubber tube carefully detached with the left hand. The lower end is then touched outside with a dry vessel to remove the small amount of adherent liquid and the bottle placed centrally under

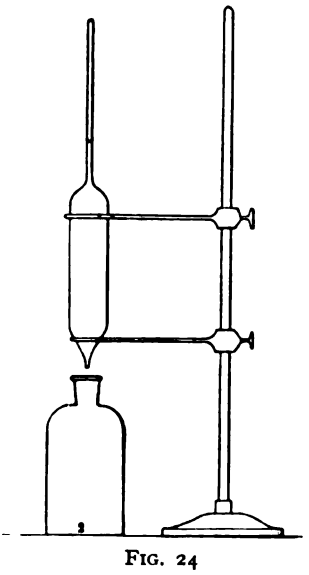

FIG. 24

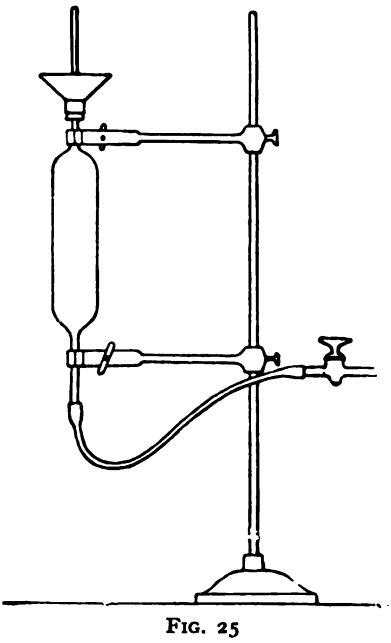

FIG. 25

the pipette. The finger is then withdrawn from the top and all the liquid flowing in a continuous jet, but not the drops falling subsequently, allowed to run into the bottle.

The pipettes should be kept perfectly free from grease and, before use, should be washed at least twice with the solution to be measured.

3. A shaking apparatus, which may be one of those commonly employed in chemical laboratories for bottles. In assayers' laboratories special closed forms of apparatus are used to protect the bottles from the action of the light. They take 10 bottles at a time and are often, as in the Mint at Rome, worked electrically. The shaking should be rapid and vigorous.

4. A kind of tray with cells for carrying 10 bottles, screened from the light, from one part to another of the laboratory.

5. A water-bath for heating the bottles during the attack of the metal.

Assaying laboratories have also a suitable bench fitted with a back and a raised ledge placed against a window, facing north if possible. On the bench the sodium chloride solution is measured, while the solutions which have already cleared are arranged on the ledge to receive the weaker standard

salt solution. By raising each test separately above the screen so that the upper part becomes directly illuminated it is easy to discern the cloud produced by the new addition of solution.

*Reagents.* 1. *Standard salt solution*, 100 c.c. of which precipitates almost completely 1 gram of pure silver. It is prepared by dissolving 5·4200 grams of pure sodium chloride to 1 litre with distilled water or 5·570 grams of sea-salt, dried between filter papers, to 1 litre with ordinary water [1] and, in the latter case, filtering the solution.

2. *Weak standard salt solution*, one-tenth as strong as the preceding solution, from which it may be prepared by dilution; or 0·5420 gram of pure sodium chloride may be dissolved to 1 litre. This solution, 1 c.c. of which corresponds with 0·001 gram Ag, is stored in a bottle fitted with a rubber stopper traversed by a pipette graduated from 1 to 5 c.c.

3. Pure nitric acid, D 1·2, free from chlorine.

*Standardisation of the salt solution.* 1 gram of pure silver (fine silver, *see* preceding method) is weighed with the greatest accuracy [2] and heated in a water-bath in one of the test bottles with 8–10 c.c. of nitric acid (D 1·2) until the metal is dissolved and the red vapours have disappeared. After cooling, the neck of the bottle is washed with a few drops of water and 100 c.c. of the standard salt solution introduced by means of one of the pipettes described, care being taken that only the liquid falling in a continuous stream enters and not the subsequent drops. The bottle is then stoppered and shaken for about 10 minutes in the shaking apparatus, the precipitate clotting and the liquid becoming quite clear. With a rapid shake the particles of precipitate are removed from the upper part of the bottle, the latter being then placed on the bench, the stopper removed and 1 c.c. of the weaker standard salt allowed to flow gently down the side of the bottle. After 4–5 minutes the bottle is raised so that the upper portion of the liquid becomes illuminated, fresh precipitation of the silver in the form of a cloud at the surface of the liquid being usually observed.

The solution is exact when this cloud is barely perceptible and when it disappears on gently shaking the liquid; if there is too much cloud, the standard solution must be corrected by addition of salt, whilst, if no cloud is produced, the solution must be diluted. Only the first case will be considered, as the second may be reduced by suitable dilution to the first. When the addition of 1 c.c. of the weaker standard salt produces too intense a cloud, the bottle is shaken in the apparatus for 10 minutes and, after clearing, treated with a further 1 c.c. of the weaker salt. This process is continued until such an addition causes either no further precipitation or only a scarcely perceptible cloud. In calculating the correction, the last c.c. is either neglected or taken as only 0·5 c.c. in the first case, but must be taken into account in the second case. If, for instance, the complete

[1] In assaying laboratories sea-salt is usually employed and 10 litres of solution prepared at a time.

[2] To facilitate weighing, strips of the rolled metal weighing more than 1 gram are placed on the balance pan, the excess being then removed first with metal shears and then by rubbing one of the strips (the largest) held in flat-ended tongs against a very fine file until perfect equilibrium of the balance is attained. The filed piece should be dusted with a brush to remove any adherent filings.

precipitation of 1 gram of fine silver requires 100 c.c. of the standard salt plus 3 c.c. of the weaker standard salt solution, to every 100 c.c. of the standard salt it will be necessary to add a quantity of sodium chloride corresponding with that contained in 3 c.c. of the weaker standard, i.e., (0·000542 × 3) gram if pure salt has been used, or (0·000557 × 3) gram with sea-salt. After this new quantity of salt has been added and dissolved, the resulting solution is tested to ascertain if any small correction is still necessary.

The temperature of the standard solution, corrected in this way, is noted. Each time it is used, it should be well shaken to render it homogeneous.

*Actual test.* We will suppose that the preliminary test of an alloy of silver and copper by Volhard's method gives the approximate fineness 834. A weight, 1·201 gram, is taken, this containing very slightly more than 1 gram of silver. Two pieces, each of this weight, are placed in two of the bottles and treated with 8–10 c.c. of nitric acid (D 1·2) with the precautions mentioned above. When cold, 100 c.c. of the standard salt solution is run into each bottle, which is then shaken, the further procedure being as described for the standardisation of the salt solution. If, in addition to the 100 c.c. of the standard salt solution, 1 c.c. of the weaker standard is required, the amount of the silver in the 1·201 gram of the sample will be 1·001 gram, the fineness of the alloy being 833·4 (1201 : 1001 :: 1000 : 833·4).

To obtain greater accuracy, the weaker standard salt solution may be added in portions of 0·2 c.c. A practised observer, however, by comparing the intensity of the cloud given by the check with that given by the sample, can estimate accurately by the eye 0·1 c.c. of the weaker standard salt solution. In special works dealing with this subject, tables compiled by Gay-Lussac are given which render unnecessary the calculations. If it happens that the addition of 1 c.c. of the weaker standard salt produces no cloud, it is best to repeat the test with a larger quantity of the sample.

Gay-Lussac's method, although expeditious, is undoubtedly the most exact of all and is universally employed for the control of silver coinage. Naturally the accuracy of the results depends on the accuracy of the weighing and particularly on the accuracy with which the standard solution is measured (1 drop = 0·5 milligram Ag). It is necessary also to allow for variations of temperature, since at different temperatures the amount of sodium chloride contained in 100 c.c. of the standard solution varies appreciably (1° higher or lower may introduce an error of about 0·2 in the fineness). To eliminate this cause of error, Gay-Lussac tried weighing the standard solution instead of measuring it, but found this procedure so much less expeditious that he discarded it and compiled a table giving corrections for temperature. In practice the simplest means of avoiding such an error is to carry out, at the same time as the test on the alloy, a control test with pure silver.

In connection with this method it is also to be borne in mind that silver chloride, as pointed out by Mulder,[1] is not absolutely insoluble, a minimal quantity remaining in solution and undergoing precipitation only by excess of the reagent. Thus, if the amount of sodium chloride exactly sufficient to

[1] *Die Silberprobiermethode.*

precipitate all the silver has been added to a solution of silver in nitric acid, a cloud will be formed in the liquid by addition of either sodium chloride or silver nitrate. This may constitute a source of error if, as Gay-Lussac originally suggested, a weak standard silver nitrate solution is used in cases where the amount of sodium chloride added is in excess with respect to the silver dissolved. On this account Stas [1] proposed a modification of the Gay-Lussac method, this consisting in the replacement of the sodium chloride solutions by the corresponding hydrobromic acid solutions, silver bromide being perfectly insoluble. This method, which is used in the Brussels mint, is rather more delicate than that of Gay-Lussac, but it requires perfect expulsion of the nitrous vapours and special precautions to prevent access of light to the tests, etc.

If, however, the Gay-Lussac method is carried out as described above, the weak standard silver nitrate being suppressed and identical conditions employed in both control test and that on the sample, all causes of error are eliminated.

As regards the influence of extraneous metals, it must be borne in mind that mercury affects the accuracy of the results, as it also is precipitated as mercurous chloride ; when this metal is present, it is expelled by heating the alloy to fusion in a graphite crucible. When tin, antimony or bismuth is present, an opalescent liquid is obtained in which it is difficult to observe the formation of cloudiness. In presence of antimony or bismuth a little tartaric acid (1–2 grams) is added, whilst when the alloy contains tin or a large proportion of lead, it is advisable to dissolve it in sulphuric acid. Further, gold in proportion exceeding a fineness of 60–80 (6–8%) influences the results as it withholds a little silver. Copper in amount greater than 50% gives coloured solutions, which render observation difficult.

**2. Determination of the Gold.**—In a flask with a long, narrow neck, 10 grams of the sample are dissolved in 80–100 c.c. of nitric acid (D 1·2), the solution being decanted off and the residue again boiled with nitric acid, which is also decanted. The residue is washed repeatedly with hot water by decantation and the undissolved gold remaining as a black powder collected in a refractory, unglazed crucible (*see* Gold and its Alloys—Quartation), dried, ignited and weighed.

**3. Detection of Tin, Antimony, Copper, Bismuth and Lead.**—5 grams of the sample are treated with nitric acid (D 1·2). In presence of tin or antimony, the liquid is opalescent or contains a slight white precipitate. If the filtered solution is rendered alkaline with ammonia, it will turn more or less intensely blue if copper is present, whilst a flocculent precipitate will form in presence of bismuth or lead, which may be identified by the usual means.

***

Natural and crude silver often contains small quantities of gold, lead, mercury, copper, antimony, arsenic and sometimes selenium and bismuth. The presence of bismuth is extremely harmful, alloys made with silver containing only traces of bismuth being rough and brittle. Refined silver is usually very pure, the best qualities containing, on the average, 99·9% Ag.

Silver is used especially alloyed with copper for jewellery, coinage, etc. The legal standard for Italian 5-lire pieces is 900 fine with a variation of 2 either way, and that for plate is usually 900 fine, and that for jewellery 800 or even less—down to 500 fine.

[1] De Koninck : *Traité de chimie analytique*, II, p. 561.

## GOLD AND ITS ALLOYS

The more important commercial products are: gold in bars, sheet, granules, powder, etc., and its alloys with copper alone and with silver and copper.

## GOLD

The essential determination to be carried out on the metal is that of the gold, the fineness being the amount of gold per 1000 parts of the metal. This determination is made as in alloys of gold and copper (*q.v.*).

## ALLOYS OF GOLD AND COPPER

The most important determination is:

**1. Determination of the Gold.**—By cupellation in presence of lead, the gold is separated from copper and other ordinary metals with which it may be alloyed, but not from silver, which resembles gold in being unoxidisable at the highest temperatures. To eliminate the silver, which always accompanies gold in larger or smaller proportion, it is necessary to treat with acid. Experience has shown that, for the complete elimination of the silver, the latter must be in considerable excess, namely, about 3 parts to 1 part of gold. It is, therefore, necessary, *before cupellation* to add silver to make this relation hold. The assay of gold hence comprises two distinct operations:

(1) Cupellation in presence of lead and silver to eliminate the base metals and to form the alloy of gold and silver in the above proportions, an operation termed *inquartation*, since the gold constitutes about one-fourth of the resulting alloy.

(2) Treatment of the latter with acid to remove the silver, this operation being known as *parting*.

To calculate the quantities of silver and lead to be used in the cupellation the gold content of the sample must be known approximately. It is necessary, therefore, to make a preliminary assay and this is usually done by means of the touchstone.

PRELIMINARY TOUCHSTONE ASSAY. This consists in tracing a streak with the sample on the touchstone beside streaks traced with gold-copper alloys of known fineness and comparing the colours of the streaks before and after treatment with acid.

This test requires:

(1) *The touchstone.* A good stone should be unattackable by acid and should be of a uniform black colour, hard, of fine grain and opaque surface.

(2) *The needles*, consisting of small, thick discs or plates of gold-copper alloys of definite fineness, fixed to metallic handles on which the fineness is marked.

(3) *The acids*, which vary in composition according to the fineness of the alloy to be tested. The acids generally used are the so-called 500 acid

for finenesses between 350 and 500, the 750 acid for finesses 500–750, and the 900 acid for finenesses above 750. The compositions of these acids are :

| 500 acid. | 750 acid. | 900 acid. |
|---|---|---|
| Nitric acid (D 1·384), 40 c.c. | Nitric acid (D 1·346), 98 c.c. | Nitric acid (D 1·384), 40 c.c. |
| Hydrochloric acid (D 1·19), 0·5 c.c. | Hydrochloric acid (D 1·171), 2 c.c. | Hydrochloric acid (D 1·19), 5 c.c. |
| Distilled water, 20 c.c. | Distilled water, 25 c.c. | Distilled water, 15 c.c. |

The *procedure* consists in rubbing the sample on the stone so as to leave a sharp line 3–4 mm. wide and 15–20 mm. long, and quite close to this, two streaks with two needles one less and the other more fine than the external characters of the alloy would indicate for it. The streaks are observed in the light and compared. A little of the acid corresponding with the fineness of the comparison needles is then rubbed with a glass rod over the streaks, which are then compared, dried with absorbent paper, again treated with acid, again dried, and the residues of gold on the stone compared. From the colour of the streaks before treatment with acid and the intensity of those remaining after the action of the acid, the approximate fineness of the alloy is judged. If the streak left by the sample is not comparable with those of the needles, the test must be repeated with needles of higher or lower fineness.

ACTUAL TEST. *Apparatus and reagents.* (1) A muffle furnace, cupels, and a thermo-electric couple like that used in the cupellation of silver (*q.v.*).

(2) Silver of 999 fineness absolutely free from gold, and lead which need not be free from silver.

(3) Highly resistant pear-shaped flasks with stout, very long necks (assay flasks) and a crucible of very fine refractory earth or of unglazed porcelain or graphite.

*Amounts of silver and lead to be used in the cupellation.* The assay of the gold is carried out in duplicate on 0·5 gram of the sample, and the amount of silver to be added for the inquartation is about three times (more exactly 2·5 times) that of the gold. Thus, if the touchstone assay indicates an approximate fineness of 900, the amount of silver to be added to each 0·5 gram of the alloy is $0{\cdot}9 \times 2{\cdot}5 \times 0{\cdot}5 = 1{\cdot}125$ gram. The silver, which is weighed to the nearest centigram, should be in sheet which is not too thin, so that the piece used in each case forms two squares of 0·5 cm. side.

The amount of lead required is also related to the fineness of the alloy and is given by the following table :

| Fineness of the sample. | Amount of lead (grams) required per 0·5 gram of sample. |
|---|---|
| 1000 | 0·5 |
| 900 | 5·0 |
| 800 | 8·0 |
| 700 | 11·0 |
| 600 | 12·0 |
| 500 | 13·0 |
| 400–100 | 17·0 |

***Procedure.*** The gold is sampled in the manner indicated for silver (*q.v.*),

reduced to sheet and two test-pieces of 0·5 gram each weighed with the greatest exactitude; if possible, each piece should consist of a single square of about 0·5 cm. side. This is placed between the two pieces of silver foil and the whole wrapped in a piece of white paper or of thin lead foil (allowing for the weight in calculating the lead to be taken) and placed in the tray beside the corresponding quantity of lead.

Meanwhile the furnace is started and the cupels, from which the dust has been blown, introduced. In gold assay there is no danger of sensible loss owing to volatilisation, so that a rather higher temperature than for silver may be used. According to T. K. Rose,[1] the most suitable mean temperature is about 1070°, each 5° above this causing a loss of 0·01 on the fineness. When the temperature indicated is reached, each cupel is charged with the weighed quantity of lead, which rapidly melts, becomes covered with a layer of oxide and, after a few instants, becomes uncovered, i.e., shining. With great care, to avoid spurting, the little parcel of sample and silver is placed in the cupel. The phenomena of the cupellation are identical with those observed with silver; after some time the agitation

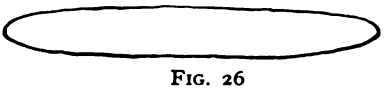

FIG. 26

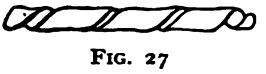

FIG. 27

on the surface is observed, then the iridescence, and finally the bright flashing. The cupels are then moved towards the door of the muffle, allowed to cool somewhat and withdrawn, the buttons being detached with a suitable utensil. With successful cupellation, the buttons should be hemispherical, shining and white at the upper part and opaque white at the lower. The button is held in strong pincers, the edges struck with a hammer and the flat part freed from cupel dust by means of a stiff brush. It is then placed on a clean anvil and struck alternately on the sides and on the flat part so as to give it a somewhat elongated form and is next reheated to redness by leaving it for a short time on a cupel in the front part of the muffle. When cool, it is rolled to obtain a strip (*fillet*) about 0·5 mm. thick and of the form shown in Fig. 26. This strip, bent in two in a smooth curve, is again reheated to redness for 4-5 minutes on a cupel. When cold, it is twisted into a spiral round a glass rod so as to obtain almost a tube about 0·5 cm. wide (*cornet*), care being taken that the rolls of the spiral do not touch (Fig. 27); this is then subjected to the operation of parting.

*Parting.* Each of two assay flasks is charged with 25–30 c.c. of nitric acid (D 1·2) absolutely free from chlorine, nitrous fumes and selenic acid, this being heated to boiling and the two cornets introduced. The heating is continued so as to maintain the liquid in gentle ebullition for ten minutes after evolution of nitrous vapours ceases.[2] After a short rest, the liquid

[1] *Journal of the Chemical Society*, 1893, LXIII, p. 707.

[2] In assay laboratories, there is usually a special apparatus for the elimination of the nitrous vapours and acid fumes evolved during the treatment of the cornet with nitric acid. It consists of one or two series of 8–10 small bunsen burners, over which are placed as many flasks with their inclined necks projecting through a rectangular aperture into a space communicating with an efficient draught chamber. Between

s carefully decanted off as completely as possible without allowing the ornet to escape. The residue is again boiled for 10 minutes with 20 c.c. of nitric acid (D 1·3). With the more concentrated acid the boiling is less egular and dangerous bumping may occur, and some authorities recommend he addition of a scrap of wood charcoal or a completely charred pepper-corn. After this second portion of acid has been decanted off, a further quantity of 20 c.c. of nitric acid (D 1·3) is added and boiled for 10 minutes to remove the last traces of silver. When this last acid together with the piece of charcoal have been removed, the cornet is washed with two quantities of 30–40 c.c. of boiling water, the flask being subsequently filled completely with cold distilled water. The mouth of the flask is then closed by means of an inverted crucible of refractory earth or unglazed porcelain, which is pressed firmly on while the flask is inverted. A little water descends into the crucible and forms a hydraulic seal, while the brittle and slender cornet slowly falls to the bottom of the crucible. After some time, when any small fragments detached from the cornet have been deposited, the flask is gradually raised to the edges of the crucible, displaced a little laterally and with a rapid movement brought into an erect position. The water is decanted from the crucible which is dried on the platform of the furnace and subsequently heated to redness in the muffle for 2–3 minutes. Under the influence of the heat the cornet contracts to about one-third of its original volume and assumes a golden-yellow metallic appearance. When cold, the two cornets are weighed together, the total weight giving directly the fineness of the sample; the weights of the separate cornets should not differ by more than 0·5 milligram.

In the assay of gold by cupellation, small losses occur (according to Rose, 0·5–1 on the fineness) owing partly to volatilisation of the gold and partly to imbibition by the cupel. This slight loss is, however, compensated by the small amount of silver (0·75–1 one-thousandth) which always remains with the gold in spite of the different treatments with nitric acid. Thus, according to Rose, if the operation is properly conducted, the error should not exceed $\pm$0·2 per thousand. The losses by volatilisation increase with the amount of lead used and, consequently, with diminution of the proportion of gold in the alloy; on this account, Riche advises the omission of the third treatment with nitric acid in the case of gold-copper alloys of lower fineness than 800. In some laboratories the small errors are estimated by making a control assay with pure gold [1] and pure copper in about the same proportions as in the sample, the mixture being cupelled with the same quantities of silver and lead, and the parting carried out under the same conditions. In assaying commercial fine gold Riche advises the addition of 20 per thousand of copper to prevent brittleness in the button obtained.

As regards extraneous metals, small quantities of platinum render the

one series and the next are the bottles with the nitric acid and the distilled water and below them three bottles to receive: (1) the first two lots of acid, rich in silver nitrate, (2) the third lot of acid, and (3) the wash water.

[1] For the preparation of pure gold, *see* Roberts-Austen: *Fourth Mint Report, London*, 1873, 46.

button wrinkled and crystalline, but less than 2% of platinum does not influence the results since, in presence of silver and gold, it then dissolves in the nitric acid. If the platinum is present in higher proportions (up to 10–15%), the cupellation is carried out at a higher temperature in presence of twice as much lead as is indicated in the table; after the parting the cornets are weighed, again subjected to inquartation with silver and 20 per 1000 of copper and again parted with acid of D 1·3, these operations being repeated until the cornets are of constant weight.

Palladium has no injurious effect, since it dissolves completely in nitric acid.

Iridium causes the formation of black spots on the button, these remaining even after parting. If the gold is dissolved in aqua regia, the iridium remains undissolved and may be collected and weighed.

## ALLOYS OF GOLD, SILVER AND COPPER

In the assay of these alloys, three cases are distinguished:

(1) Rich alloys, in which the proportion of gold to silver is higher than 1 : 3.

(2) Medium alloys, with a proportion of about 1 : 3.

(3) Poor alloys, with a proportion less than 1 : 3. The assay of these alloys includes two operations:

(1) Cupellation, which gives the gold and silver together.

(2) Parting, which gives the gold alone.

Preliminary test. In presence of silver the touchstone assay does not always give reliable results (the presence of silver is easily detected by the formation of a slight, white precipitate on the streak when treated with the acid), so that a preliminary assay by cupellation is advisable. This is made with 0·250 gram of the sample and 4–8 grams of lead, according to the supposed richness in copper, the button of gold and silver being weighed; the weight of the sample, less that of the button, gives approximately that of the copper. The button is then rolled, the strip treated with nitric acid and the remaining gold weighed; the proportion of silver is then found by difference.

I. Rich Alloys. (*a*) *Determination of the gold.* This is carried out on two separate portions of 0·5 gram under the conditions given for the determination of gold in gold-copper alloys. The inquartation silver must be diminished in amount by the approximate silver content indicated by the preliminary assay (*see* p. 287). The amount of lead required is based on the total fineness and on the ratio between the gold and silver (*see* later: *Medium Alloys*).

(*b*) *Determination of the silver.* 0·5 gram of the alloy is cupelled with the quantity of lead used for the determination of the gold, the resulting button representing gold and silver together; the latter is thus found by difference.

If the alloy consists of gold and silver alone, 20-thousandths of copper must be added to the test. If the gold fineness is less than 800, the third treatment with acid is omitted.

II. MEDIUM ALLOYS. (*a*) *Determination of the gold and silver.* Two quantities of 0·5 gram are cupelled under the conditions given for gold-copper alloys but at a somewhat higher temperature, and with no added silver. The amount of lead to be added is calculated on the basis of the total gold and silver contents, one-fourth of the quantity indicated by the table for the cupellation of gold and three-fourths of that given for the cupellation of silver, being taken.

Example: If the preliminary assay gives Au 220 and Ag 680 per 1000, the total fineness is 900. For this value the table for the cupellation of gold would indicate 5 grams of lead, so that 1·25 is taken, and the table for the cupellation of silver would indicate 3·5 grams of lead, so that 2·6 ($= 3 \times 3{\cdot}5/4$) is taken; the total amount of lead taken is thus $1{\cdot}25 + 2{\cdot}6 = 3{\cdot}85$ grams.

The buttons obtained are weighed together and subjected to parting. The gold is given by the total weight of the two cornets and the silver by difference (button minus gold).

III. POOR ALLOYS. Two 0·5 gram samples are cupelled as described for the cupellation of silver and with the amounts of lead there prescribed; the temperature is, however, kept somewhat higher, especially if the fineness of the gold exceeds 50 per thousand. The sum of the weights of the two buttons gives the silver + gold. To separate the silver, the buttons are parted, bearing in mind that, if the fineness of the gold is not more than 5 per 1000, the two buttons should be parted in the same flask, and that, for values exceeding 20 per 1000, the buttons should be rolled and reheated at low redness; further, that, before decanting the acid from the flask, the liquid should be given a rotary motion, so that the gold dust collects at the bottom; that the third treatment with acid should be omitted and that great care is necessary to avoid loss during the descent of the gold dust into the crucible.

If the gold content does not exceed 60–80 per 1000, the silver may be determined with greater exactitude by the Gay-Lussac method (*see* Silver and its Alloys).

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*Crude gold* contains considerable quantities of impurities, especially silver, copper, lead, bismuth, tin, antimony, arsenic, etc. Thus, gold obtained by amalgamation varies from 865 to 970 fine, whereas that given by the Siemens process has a fineness of 890–900 and contains, besides silver, only traces of copper and lead; gold precipitated by zinc is 600–700 fine and contains considerable proportions of zinc, lead, iron and copper.

*Refined gold* reaches the fineness 993–999, but always contains small quantities of silver.

Gold is used more especially alloyed with copper for jewellery, coinage, medals, etc. The *legal fineness* of the *Italian gold coinage* is 900 ± 1 and that of British coinage 916·66. With jewellery, plate, etc., the fineness may vary from 920 to 500.

Gold-silver and gold-silver-copper alloys are also largely used, more especially to obtain special effects in articles of jewellery (green gold: 750 Au, 250 Ag; red gold: 750 Au, 200 Ag, 50 Cu; white English gold: 750 Au, 170 Ag, 80 Cu, etc.).

# METALLIC COATINGS

Many metallic objects are coated, either to render them more resistant to the action of external agencies or to enhance their appearance, with more or less thin layers of other metals or of oxides. These coatings are easy to characterise by the tests given below.

## GOLD-PLATING

### (Gilding)

**1. Technical Test.**—The surface of the object is rubbed repeatedly with a small piece of very fine glass paper (No. 000) so as to concentrate any gilding at one point of the glass paper. This point is then treated with a drop of conc. nitric and one or two drops of conc. hydrochloric acid and warmed gently over a very small flame until the metal is dissolved. The solution is then washed into a test-tube with 1–2 c.c. of water, the liquid being filtered if turbid and heated with either an equal volume of fresh sulphur dioxide solution or a few drops of fresh stannous chloride solution. In presence of gold, a violet red, varying coloration is observed owing to the formation of purple of Cassius

**2. Test for Small Objects.**—The sample, or part of it, or a number of small pieces, according to circumstances, are heated on the water-bath with nitric acid diluted with an equal volume of water. When the attack of the common metal is complete, the liquid is filtered through a small filter and the residue washed thoroughly with hot water. The filter is then incinerated in a porcelain dish or crucible and the ash treated with 2 drops of conc. hydrochloric acid and 1 drop of conc. nitric acid and evaporated to dryness on a water-bath until the excess of acid is entirely expelled. When cold, the residue is taken up in about 2 c.c. of distilled water and filtered, the filtrate being heated to boiling with an equal volume of sulphur dioxide solution or of a saturated oxalic acid solution or a few drops of stannous chloride solution. If gold is present, the characteristic violet-red coloration of purple of Cassius is observed.

**3. Test for Large Objects.**—After removal of any organic matter, the surface is scraped with a penknife and the scrapings submitted to the preceding test.

## SILVER-PLATING

**1. Technical Test.**—The article to be tested, freed from grease,[1] is touched with a drop of conc. nitric acid and the latter absorbed by a strip of filter-paper. The spot is then treated with a drop of formaldehyde solution (commercial formalin) and a drop of 20% sodium hydroxide solution. In presence of silver, a blackish spot of reduced silver forms either immediately or after some time.

[1] Sometimes objects are covered with a varnish which has nitro- or acetyl-cellulose as its base and can be removed only mechanically.

**2. Test for Small Articles.**—After being freed from grease, the article or part of it or a number of small pieces, are treated with 8–10 drops of a mixture of 9 vols. of conc. sulphuric acid with 1 vol. of conc. nitric acid—a mixture which readily dissolves the superficial silver but attacks the metal underneath either not at all or but little. When the attack is over, the acid is decanted into a test-tube, mixed with 2–3 c.c. of water, filtered if necessary and divided into two portions. To one of these are added 1–2 drops of dilute hydrochloric acid, which are allowed to flow gently down the wall of the tube and form a layer on the surface of the sulphuric acid solution. If silver is present, a more or less distinct milkiness is observed —best by comparison with the other portion—at the surface.

**3. Test for Large Articles.**—In general the technical test (*see* above) is applicable in this case. If, however, the surface or form of the object renders this difficult the surface or a few scrapings may be treated with nitric acid diluted with an equal volume of water, care being taken to stop the action as soon as the superficial silver coloration disappears. The nitric acid solution is then decanted into a dish and evaporated to dryness with a drop of dilute hydrochloric acid on a water-bath. The residue is taken up in hot water, acidified with nitric acid and filtered through a small, very compact filter, which is repeatedly washed with hot water. A small quantity of hot, dilute ammonia is then passed a number of times through the filter and the ammoniacal solution divided into two parts, one of which is made faintly acid with nitric acid. In presence of silver a slight precipitate or a more or less marked milkiness is observed.

## NICKEL-PLATING

**1. Technical Test.**—The surface of the article is treated with a drop of conc. hydrochloric acid, a crystal of methylamine hydrochloride being placed close by and heat applied. In presence of nickel, the place attacked by the acid exhibits a blue spot which disappears on cooling.

**2. Dimethylglyoxime Test** (highly sensitive).—After being freed from grease, the surface of the object is moistened with one or two drops of nitric acid diluted with an equal volume of water, the acid being subsequently washed into a test-tube, rendered alkaline with ammonia, heated to boiling, filtered if necessary and treated with two or three drops of 1% alcoholic dimethylglyoxime solution. In presence of nickel, a red precipitate or at least a pink coloration is formed.

If this test is applied to an object of copper or brass, a little of the latter in the solution would give a brown coloration and thus mask the nickel reaction. In such case, after addition of the glyoxime and gentle heating, the liquid is filtered ; if nickel is present, a slight red precipitate will remain on the filter. A better method to follow under these circumstances consists in acidifying the ammoniacal solution with hydrochloric acid, precipitating the copper by means of hydrogen sulphide, filtering, eliminating the excess of hydrogen sulphide, rendering slightly ammoniacal, filtering if necessary, and then adding the alcoholic dimethylglyoxime.

## TIN-PLATING

The surface of the object or scrapings from it are treated with hydrochloric acid diluted with an equal volume of water and gently heated. The liquid is filtered and treated with a drop of mercuric chloride solution, a white or grey precipitate of calomel or metallic mercury being formed in presence of tin.

## ZINC-PLATING

The surface is heated gently with dilute sulphuric acid and the solution transferred to a beaker and treated with hydrogen sulphide. The filtered liquid is freed from the excess of hydrogen sulphide, treated with a little ammonium chloride, rendered faintly alkaline with ammonia, boiled, and again filtered. To the filtrate, acidified with acetic acid, potassium ferrocyanide is added. In presence of zinc, a dirty white flocculent precipitate forms either immediately or after some time.

## LEAD-PLATING

Scrapings of the surface are treated in a dish with nitric acid, evaporated to dryness and taken up in a few drops of water. The solution is tested for lead by means of potassium chromate or iodide.

## ALUMINIUM-PLATING

The surface, or scrapings of it, are heated with 10% sodium hydroxide solution. The liquid is diluted somewhat, filtered, acidified with hydrochloric acid and made alkaline with ammonia. A white gelatinous precipitate is formed in presence of aluminium.

## COPPER-PLATING

### (on Iron)

The object or part of it is treated in the cold with conc. nitric acid, which dissolves the copper but scarcely affects the iron. The solution is decanted off, diluted and tested for copper with ammonia.

## BRASS-PLATING

The surface is treated with nitric acid diluted with an equal volume of water, the liquid being filtered and rendered alkaline with ammonia: the characteristic blue coloration of copper in ammoniacal solution is observed. The liquid is then acidified with hydrochloric acid, treated with hydrogen

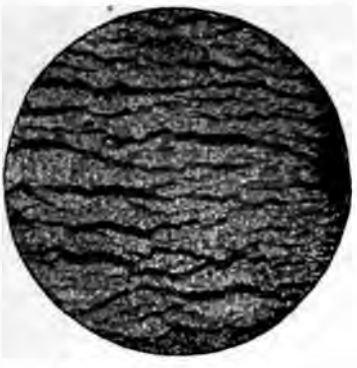

FIG. 28. German sheet

FIG. 29. English sheet

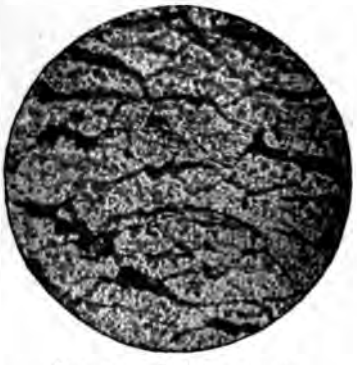

FIG. 30. Belgian sheet

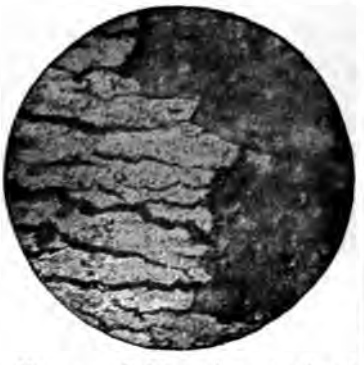

FIG. 31. Belgian sheet (at bend)

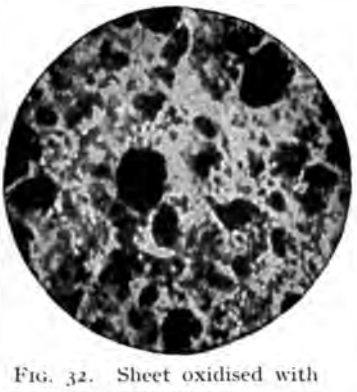

FIG. 32. Sheet oxidised with reagents

FIG. 33. Sheet oxidised with reagents (at bend)

[To face p. 295.

sulphide, filtered, boiled to expel excess of hydrogen sulphide, made alkaline with ammonia, heated and filtered. In the filtrate, acidified with acetic acid, the zinc is tested for with potassium ferrocyanide.

## OXIDISING

For increased protection against atmospheric agencies or for the sake of appearance, many objects are coated either chemically or mechanically with a thin layer of oxide, which imparts to them a brown or bluish-brown coloration.

Similar coloration may, however, arise spontaneously during the working of the objects owing to reheating and it is not always easy to decide if the oxidation is artificial or spontaneous. One distinguishing character is the regularity and uniformity of the layer of oxide with artificially oxidised objects, in comparison with the irregularity of layers of oxide formed spontaneously; the following tests are based on this criterion.

**1. For Copper and Brass Objects.**—The surface of the object is thoroughly freed from grease by means of benzene and treated with a drop of 5% mercuric chloride solution. If the layer of oxide is very regular and compact, the reagent will not get into contact with the metal and no reaction will be observed. If, however, the oxidation is irregular, the mercuric chloride undergoes reduction at the surface of the metal, forming a grey spot.

**2. For Objects of Iron.**—After being cleaned with benzene, the oxidised surface is moistened with a drop of 5–6% copper sulphate solution. If the oxidation is irregular and hence not artificially formed, a spot of metallic copper appears either immediately or after some time, whereas, if the oxidation is regular and uniform, any reduction which may occur will be observable only after the lapse of a long period.

With reference to this test it is, however, to be noted that sheet metal (*lamière bleu-lisse*) is now put on the market covered with a regular layer of ferroso-ferric oxide of a bluish colour, which, although obtained during the process of rolling is very regular and uniform and does not allow of any reduction of copper sulphate.

Such sheet is nevertheless readily distinguishable from that oxidised by means of reagents or the like.

1. *Technical test.* When a sheet of this character is bent at right angles it sheds its oxide at the bend in the form of scale and shows the naked metal, whereas sheet oxidised by reagents exhibits little change.

2. *Microscopic test.* Further, microscopic examination, in reflected light and under a magnification of 100–120 diameters, of the surface of such sheet reveals numerous minute fissures which have been made in the oxide during rolling and lie parallel to the axis of the rolls. Figures 28, 29 and 30 (*see* plate) represent reproductions of microphotographs of the surfaces of three types of such sheets from Germany, England and Belgium, while Fig. 31 shows the appearance of a Belgian sheet at the bend.

Metal which has been oxidised with reagents exhibits no such parallel

cracks, but numerous small rounded pittings produced by the corrosive action of the reagent used to obtain the oxidation. Fig. 32 is a reproduction of the microphotograph of the surface of a sheet oxidised with reagents and Fig. 33 that of the surface of the same sheet near a bend; the different behaviour in this case is obvious.

## CHAPTER VI

# FUELS

Leaving aside wood, which is rarely examined as to its value as a combustible, the fuels used industrially are mainly *coal, charcoal* and *mineral oils* ; the last will be considered later. The coals are distinguished according to the degree of carbonisation as *peat, lignite, bituminous coal* and *anthracite.* Extensive use as a fuel is also made of *coke,* the residue of the dry distillation of bituminous coal, the volatile products being illuminating gas, ammonia and tar. *Fuel-blocks* (briquettes) are also largely used at the present time ; these are obtained by the compression in moulds of fragments of different coals, usually with the addition of cementing materials. In this way waste coal may be utilised and coal which is inconvenient to use on account of its physical condition rendered more useful.

The quality and technical value of coal are determined by *chemical analysis* and *calorific examination.* The methods adopted are the same for all coals and are described below under the heading : General Methods. In the special part data will then be given relating to each of the different types of coal.

In all cases, selection of the sample is of great importance.

**Sampling.**—Coal is usually far from homogeneous, and care must be taken that the sample for analysis represents as closely as possible the mean composition of the whole of the parcel to be examined. When the sample is to be taken from a mine or from a large quantity, portions are taken with a shovel from different, regularly distributed points of the mass, a large quantity being thus collected. The larger lumps of this are broken up and the whole well mixed and spread out in the form of a square and the diagonals of the latter drawn. Two opposite triangles are then discarded and the remaining two, further disintegrated and mixed, formed into another square. These operations are repeated several times until a sample of about 2 kilos is obtained, this being reduced to small pieces and stored in dry, tightly closed vessels. When, however, the laboratory is supplied with a limited sample, the whole of the latter is broken up and stored as above.

In either case, a portion of the sample thus prepared sufficient for the determinations to be made (about 200 grams) is reduced to coarse powder and stored separately in a dry, air-tight vessel. For each single determination, part of this sample is powdered to the degree of fineness requisite in each case, care being taken not to throw away any part. Consequently, when the portion taken has been powdered and sieved through the sieve

of the proper mesh, that remaining on the sieve must be again powdered and sieved until the whole has passed through.

## GENERAL METHODS

### 1. Chemical Analysis

This usually includes determinations of the moisture, ash, coke and volatile substances, and sulphur (*see* 1, 2, 3 and 4). Of interest in some cases are determinations of the phosphorus, carbon and hydrogen, nitrogen and oxygen (*see* 5, 6, 7 and 8).

**1. Determination of the Moisture.**—About 5 grams of the substance, not too finely powdered (say, to pass through a sieve of 250 meshes per sq. cm.), are dried in an oven at 105–110° to constant weight, the sample being placed in a covered platinum dish or crucible or between two watch-glasses; as a rule the drying does not require more than two hours. Since dry coal dust, especially that of highly bituminous coal and lignites, tends to oxidise in the air, any increase in weight should be neglected and the preceding weight taken as constant. In such cases, when highly exact determinations are required, the drying should be carried out in a boat in a current of carbon dioxide.

With washed coal, peat and certain earthy lignites, the determination of the hygroscopic moisture is preceded by that of the *water of imbibition.* For this purpose, a large quantity (at least 1 kilo) of the coal, coarsely ground and weighed, is left to dry in the air, the diminution in weight representing the water of imbibition. The substance thus obtained is powdered and used for determining the hygroscopic moisture and other constituents.

**2. Determination of the Ash.**—From 2 to 5 grams of substance (that used for the determination of moisture will serve) are incinerated either in a platinum dish in a muffle or in an open, inclined platinum crucible resting on a perforated asbestos card over a bunsen flame, care being taken to heat gently at first to drive off the volatile substances and to increase the temperature gradually to redness.

In some cases the ash is analysed chemically to determine its principal components and its alkalinity; it may also be examined from the point of view of its fusibility.

**3. Determination of the Coke and Volatile Substances.**—1 gram of the substance (coals rich in volatile matters are best coarsely powdered, say to pass through a sieve of 100 meshes per sq. cm.) is weighed in a platinum crucible 30–35 mm. high, which is placed covered on a triangle of platinum wire arranged so that the bottom of the crucible is 3 cm. above the apex of a bunsen burner giving a flame 18–20 cm. high. When the burner is lighted, it is placed at once under the crucible and maintained as long as luminous flames issue from the edges of the crucible; when these cease—usually after not more than two minutes—the flame is extinguished and the crucible, without opening it, placed in a desiccator, allowed to cool, and weighed. The residue in the crucible, less the ash, is regarded as coke (fixed carbon), and the loss in weight, less the moisture, as the

volatile matter (hydrocarbons and other organic substances). The appearance of the coke is noted: whether it is pulverulent, or composed of fragments more or less cemented together, or fused, and in the last case, if it is compact or porous, and more or less swollen.

**4 Determination of the Sulphur.**—The sulphur contained in fuels is present partly as sulphides (pyrites) and sulphates, and partly in organic compounds. In the combustion part of the sulphur (that of the sulphates and some of that of the sulphides) remains in the ash, whilst the remainder (the organic sulphur and part of that of the sulphides) passes over among the products of combustion (combustible, injurious or volatile sulphur) as sulphur dioxide and, in small proportion, sulphur trioxide.

The total sulphur is determined by a slight modification of Eschka's method, which is carried out as follows: About 1 gram of the finely powdered coal (passing a sieve of 650 meshes per sq. cm.) is thoroughly mixed in a roomy platinum crucible with about 1·5 gram of a mixture of magnesium oxide (2 parts) and dry sodium-potassium carbonate (1 part) by means of a platinum wire, about 0·5 gram of the same mixture being then placed on the top. The open and inclined crucible is then arranged in the hole in a piece of asbestos board and heated over a small flame so that only its lower portion is reddened. The heating is continued for about an hour—the mixture being frequently stirred with a platinum wire—until the grey colour has changed uniformly to yellowish, reddish or brown. The crucible is then allowed to cool and the contents washed with hot water into a beaker and the liquid made feebly yellow with a little bromine water, boiled, and filtered, the residue being washed with boiling water. The filtrate is acidified with hydrochloric acid, boiled to expel the remaining free bromine, and the colourless liquid precipitated with barium chloride and the barium sulphate weighed as usual.

If the fixed and volatile sulphur are required separately, the former is determined directly. To this end, a weighed quantity of the coal sufficient to give 1–2 grams of ash is incinerated and the ash treated in the hot in a porcelain dish with hydrochloric acid and a little potassium chlorate or bromine to oxidise any sulphites formed as well as the sulphides. The excess of chlorine or bromine is expelled by boiling, the liquid precipitated with ammonia and filtered, and the filtrate acidified and precipitated with barium chloride in the usual way: $BaSO_4 \times 0{\cdot}1374 = S$. Total sulphur minus fixed sulphur = volatile sulphur.

**5. Determination of the Phosphorus.**—This is carried out on the ash (1–2 grams), which is digested with conc. hydrochloric acid in a porcelain dish on a water-bath, evaporated to dryness and the residue moistened with hydrochloric acid, diluted with water, filtered into another porcelain dish and taken almost to dryness with several additions of nitric acid. The residue is then taken up in water acidified with nitric acid and precipitated in a beaker with ammonium molybdate and so on (*see* Determination of Phosphorus in Iron, p. 173).

**6. Determination of the Carbon and Hydrogen.**—These are determined by the ordinary method followed for the elementary analysis of organic substances, the substance being burnt in a current of oxygen and

in presence of copper oxide and lead chromate, copper spirals also being used. About 0·4 gram of substance, not too finely powdered, is used. At the beginning of the combustion, it is well to heat moderately and in a current of air rather than of oxygen ; when the volatile products are burnt —this being easily judged from the aspect of the coke remaining in the boat—the fixed carbon is burnt at a high temperature in a current of oxygen. If the undried substance is employed, the moisture content must be allowed for.

**7. Determination of the Nitrogen.**—This is made on 0·75–1 gram of the finely powdered sample by Kjeldahl's method (*see* Fertilisers, p. 123).

**8. Determination of the Oxygen.**—This is calculated by difference, the percentages of carbon, hydrogen, nitrogen, volatile sulphur, ash and moisture being added and the sum subtracted from 100.

## 2. Determination of the Calorific Power

The *calorific power* of a fuel, is the quantity of heat generated by the complete combustion of 1 gram of the fuel, expressed in small calories.

The *small calorie* (*cal.*) is the amount of heat necessary to raise by 1° C. (more exactly from 0° to 1°) the temperature of 1 gram of water. Some refer the calorific power to 1 kilo and use as unit of heat the *large calorie* (*cal.*), which is the amount of heat required to raise by 1° C. the temperature of 1 kilo of water ; the numbers are the same in the two cases.

In some cases also the *evaporative power* of a fuel is calculated, this representing the number of kilos of water at 0° which could be transformed into aqueous vapour at 100° by the combustion of 1 kilo of the fuel. Since each kilo of water requires 637 large calories (100 to bring it from 0° to 100° and 537 to transform it into steam also at 100°), the evaporative power is obtained by dividing the calorific power by 637.

The calorific power of a fuel may be calculated approximately from the chemical composition, but it is best to determine it directly by calorimetric methods. The calorific value is referred, according to circumstances, to the fuel as such or simply dried, or to the pure fuel (moisture and ash being deducted).

**1. Calculated Calorific Power.**—Formulæ derived from that of Dulong are used, but the results are only moderately satisfactory. According to Mahler,[1] that to be preferred is the following, which gives, with most coals, errors not exceeding 3% :

$$p = 8140C + 34500H - 3000(O + N),$$

where C, H, O and N are the respective quantities of carbon, hydrogen, oxygen and nitrogen contained in 1 gram of the pure fuel (moisture and ash deducted) and $p$ is the required calorific value, referred to the pure fuel.

By putting

$$O + N = 1 - C - H,$$

the above formula simplifies to :

$$p = 11140C + 37500H - 3000.$$

[1] *Études sur les combustibles solides, liquides et gazeux* (Paris, 1903), pp. 4 and 56.

A totally different formula which permits of the calculation of the calorific value of coals with a high degree of approximation is that proposed by Goutal,[1] namely:

$$p = 82C + aV,$$

where $p$ is the calorific power of the fuel as such, C and V are the percentages of fixed carbon (coke less ash) and volatile matter (less moisture) and $a$ a coefficient expressing the calorific power (divided by 100) of the volatile matters and varying with the amount of these volatile matters. To determine the value to be ascribed to $a$ the percentage $V^1$ of volatile matters in the fuel supposed free from moisture and ash is calculated by the formula, $V^1 = \frac{100V}{C + V}$; the corresponding value of $a$ is then obtained from the following table:

| $V^1$ | $a$ | $V^1$ | $a$ | $V^1$ | $a$ | $V^1$ | $a$ |
|---|---|---|---|---|---|---|---|
| Less than 5 | 100 | 14 | 120 | 23 | 105 | 32 | 97 |
| 5 | 145 | 15 | 117 | 24 | 104 | 33 | 96 |
| 6 | 142 | 16 | 115 | 25 | 103 | 34 | 95 |
| 7 | 139 | 17 | 113 | 26 | 102 | 35 | 94 |
| 8 | 136 | 18 | 112 | 27 | 101 | 36 | 91 |
| 9 | 133 | 19 | 110 | 28 | 100 | 37 | 88 |
| 10 | 130 | 20 | 109 | 29 | 99 | 38 | 85 |
| 11 | 127 | 21 | 108 | 30 | 98 | 39 | 82 |
| 12 | 124 | 22 | 107 | 31 | 97 | 40 | 80 |
| 13 | 122 | | | | | | |

**2. Calorimetric Determination of the Calorific Power.**—The calorimetric or direct methods are undoubtedly to be preferred to those just mentioned as they give far more certain results.

The numerous forms of apparatus devised for such determinations may be grouped in three classes: (1) calorimeters in which the combustion takes place in a stream of air or oxygen at the ordinary pressure, like those of Favre and Silbermann, Alexejew, Schwackhöfer, and F. Fischer; (2) calorimeters in which the combustion occurs with the aid of an oxidising substance mixed with the fuel, as in those of Lewis Thompson, Stohmann, and Parr; (3) calorimeters in which the combustion is effected with oxygen at constant volume and very high pressures, known as *calorimetric bombs*; the first such bomb was due to Berthelot and Vieille and on this were based the more practical and cheaper ones of Mahler, Hempel and Kroeker, which are the most suitable forms of apparatus for exact determinations.

Only the types most commonly used will be described here.

(*a*) LEWIS THOMPSON CALORIMETER. This is a very simple apparatus giving only approximate results comparable among themselves; it is, however, still in common use in England, where contracts are made on the basis of its indications. It consists (Fig. 34) of a large glass cylinder with

[1] *Comptes Rendus de l'Acad. des Sciences*, 1902, CXXXV, pp. 477–479.

a mark at two litres, and a brass foot fitted with a small cylindrical copper capsule or furnace in which the combustion occurs. The capsule is covered with a copper cylinder with a row of holes round the bottom and a tube with a tap at the top; this cylinder is held in place by four springs on the brass foot. A thermometer reading to 0·1°, and protected by a metal guard, is also required.

2 grams of the fuel, ground in an iron mortar to pass through a No. 6 sieve (650 meshes per sq. cm.), are thoroughly mixed on a piece of shining paper by means of a flexible steel spatula with the oxidising mixture (3 parts of powdered, dry potassium chlorate and 1 part of potassium nitrate, carefully mixed without using the iron mortar and passed through a No. 6 sieve), sufficient of the latter being used to give a homogeneous, lead-grey mixture, which should burn completely, regularly and moderately rapidly. The amount of oxidising mixture necessary is usually 20–30 grams per 2 grams of fuel, but it varies with the character of the fuel and should be determined by preliminary trial.

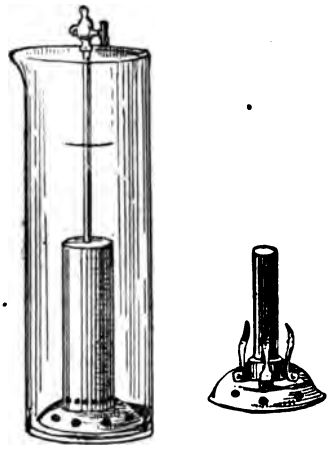

FIG. 34

By means of the spatula used before, the mixture is placed in the copper capsule in such a way as to compress it uniformly and as little as possible; if the quantity of the mixture is too great to be held by the capsule without compression, it is advisable to use only 1 gram of the fuel and the corresponding amount of the oxidising mixture. On the top of the mixture is placed a piece of slow match,[1] which should protrude about a centimetre, the copper cylinder fitted, the tap closed and the whole immersed in the water in the glass cylinder; the water should be, according to circumstances, between 2° and 7° lower than the temperature of the air.[2] The water is mixed by means of the apparatus itself and the temperature shown on the thermometer noted; the apparatus is then withdrawn, the match lighted, the cover rapidly replaced and the whole at once placed in the water before the mixture ignites. After a few seconds, when ignition occurs, the gaseous products issue turbulently from the holes in the cover and escape upward through the water.

At the end of the combustion, which, if regular, requires one or two minutes, the tap is opened, the tube unstopped by means of an iron wire and the water stirred with the apparatus, the highest temperature reached being observed. The rise of temperature, increased by one-tenth to correct approximately for the losses and for the heat absorbed by the apparatus, is multiplied by the weight of water in the glass cylinder. The product

[1] Made from cotton lighting wick (or better of de-fatted jute) immersed in concentrated potassium nitrate solution and dried in an oven.

[2] For ordinary air temperatures, the temperature of the water should be as follows:

| | | | | | |
|---|---|---|---|---|---|
| Air temperature | 10° | 15° | 20° | 25° | 30° |
| *Water temperature* | 7·9° | 11·9° | 15·9° | 19·7° | 23·2° |

represents the heat generated by the combustion of the fuel, and this, divided by the weight of the fuel, gives the calorific power sought.

The capsule should be examined to ascertain if any appreciable quantity of the coal remains unburnt. It is advisable to make several tests on each sample, the highest result obtained, and not the mean, being regarded as correct. It should be pointed out that, under the above conditions, coke and anthracite burn with difficulty, while peat and many bituminous lignites burn only incompletely.

In some Thompson calorimeters of English construction, the amount of water placed in the glass cylinder weighs 29,010 grains (1879·85 grams). When 30 grains (1·944 grams) of the fuel are burnt, since $29010 \div 30 = 967 = 537 \times 9 \div 5$, the rise in temperature in Fahrenheit degrees (increased by one-tenth) indicates directly the grains of water at 100° transformable into steam at 100° by the heat generated by one grain of the fuel, i.e., the evaporative power calculated for water at 100° and not, as usual, at 0°.

It may be pointed out that, in England, calorific powers are mostly expressed in terms of the *British Thermal Unit* (B.T.U.), which is the quantity of heat necessary to raise the temperature of 1 lb. of water (0·4536 kilo) by 1° Fahrenheit. The large calorie = 3·9683 B.T.U. and 1 B.T.U. = 0·252 large calorie. Further, a calorific power of $x$ calories per kilo corresponds with 1·8 $x$ B.T.U. per pound, or $x$ B.T.U. per pound is equivalent to 0·5555 $x$ calories per kilo.

With other Thompson calorimeters, the glass cylinder is marked at 2000 c.c. and also at 2148 c.c. (= 537 × 4). If the latter quantity of water is taken and 2 grams of the fuel are used, the rise of temperature (increased by one-tenth), multiplied by 2, will give directly the evaporative power (referred to water at 100° C. and therefore not to the standard usually adopted : *see* later).

(*b*) MAHLER BOMB CALORIMETER. This apparatus (Fig. 35), which is among the best of those employed, consists of a vessel or bomb *a* of fairly pure, forged mild steel, nickelled outside and enamelled inside : capacity about 650 c.c., thickness of walls 8 mm., weight about 4 kilos. The bomb is closed by a screwed iron lid *b* with lead packing and furnished in the centre with a ferro-nickel conical screw valve *r*. The cover supports the terminals, consisting of two platinum rods *e*, one passing through the cover and insulated from it and the other fixed directly to the cover and supporting a flat platinum dish *c* in which the fuel is placed. The two terminals are connected by a small spiral of very thin iron wire which burns on passage of the current (about 2 amps. at 8–10 volts) and so ignites the fuel in contact with it.

The bomb rests on supports on the bottom of the brass calorimetric vessel *A*, which contains 2,200 grams of water, a thermometer *t* divided into fiftieths of a degree and allowing 0·01° to be estimated, and a spiral stirrer *d*. To protect it from external influences, the calorimeter is placed inside a double-walled metallic vessel *B* filled with water and covered with felt.

To make a determination, exactly 1 gram of the fuel, not too finely powdered, is weighed into the capsule *c* and this placed in the bomb after one of the iron wire spirals has been fitted to the terminals so that it comes into contact with the fuel. The lid *b* is screwed tightly down, the valve connected with a cylinder of compressed oxygen by means of a copper

tube carrying a manometer and the bomb slowly filled with oxygen [1] until the pressure is 20–25 atmos. (or less, if the coal burns very easily). The bomb is then placed in the calorimeter *A*, into which the proper amount of water is poured, the thermometer *t* being placed in position, the stirrer *d* started and the temperature read off every minute. After five minutes, ignition is caused by the momentary passage of the current. The temperature is read half a minute after ignition, after a further half-minute, and then each minute until the maximum temperature is reached (after 3 or 4 minutes) and for five minutes during the subsequent fall in temperature.

At the end of the experiment, the tap *r* of the bomb is opened to allow the gas to escape, the bomb itself being then opened and washed out inside with a little distilled water.[2] The nitric acid formed from the nitrogen contained in the bomb is determined in the wash water by titration with caustic potash solution (1 c.c. = 0·01 gram $HNO_3$) in presence of methyl orange. Any sulphuric acid formed is also calculated as nitric acid, but with fuels poor in sulphur no appreciable error is introduced in this way. When, however, allowance is to be made for the sulphuric acid, the procedure is as follows: The wash water is heated for a short time to expel carbon dioxide and titrated with N/10-baryta in presence of phenolphthalein; excess of standard sodium carbonate solution is then added and the excess titrated with N/10-hydrochloric acid in presence of methyl orange. The volume of baryta solution used corresponds with the sulphuric and nitric acids together, and that of the sodium carbonate solution with the nitric acid alone.

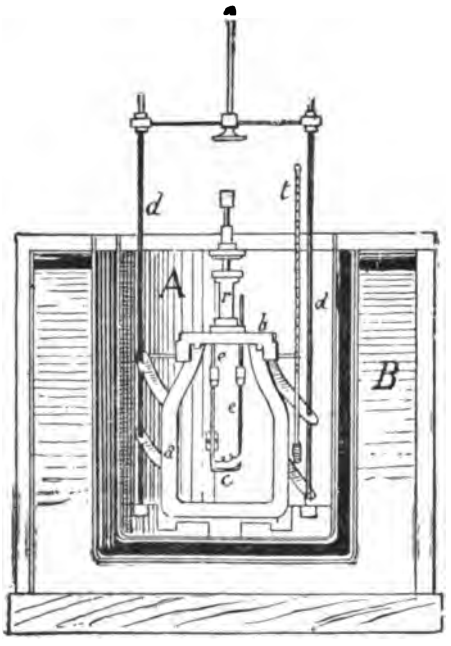


FIG. 35

In calculating the results of the measurement, it is first necessary to establish the correction necessary owing to the exchange of heat with the surrounding air in the interval of time between ignition and the attainment

[1] Compressed oxygen, if obtained electrolytically, often contains hydrogen, which appreciably alters the results of the calorimetric experiments. In such case it is necessary to purify it, before admitting it to the bomb, by passing it slowly through a red-hot copper tube and then through a coil cooled with water. On the other hand, oxygen from liquid air, containing appreciable quantities of nitrogen, has the disadvantage of giving rise to the formation of nitric acid, allowance for which must be made in calculating the results.

[2] With fuels poor in hydrogen and hence yielding little water when they burn, a few c.c. of water may be placed in the bottom of the bomb before closing it so that the products of oxidation of the nitrogen and sulphur may be dissolved.

of the maximal temperature. This correction is easily made by means of the thermometer readings before ignition and after the maximum, these giving the mean thermometric variations per minute in the preliminary and final periods. It is then assumed that, during every minute of the period between ignition and the attainment of the maximum temperature the temperature varies uniformly, so that the correction may be referred to the mean temperature of the minute considered. If the mean temperature of a definite minute differs by less than 1° from the maximum, it is held that the diminution of temperature due to loss of heat during that minute is equal to the mean diminution in every minute after the maximal temperature; if, however, the mean temperature of any minute differs from the maximum by more than 1° and less than 2°, the correction for that minute is taken as the mean diminution after the maximum temperature, decreased by 0·005°. Finally, for the first half-minute after ignition it is assumed that the variation is equal to the mean observed before the ignition.

Besides this correction, account must also be taken of (1) the heat of combustion of the iron coil, 1·6 cal. being allowed per milligram of iron, and (2) the heat of formation of the nitric acid, which is 0·23 cal. per milligram of nitric acid (also of the heat of formation of sulphuric acid; in the open air, sulphur dioxide will be formed and the correction to be subtracted is 2·25 cals. per milligram of sulphur or 0·73 cal. per milligram of sulphuric acid).

The calorific power $p$ (in the case where the sulphuric acid has been calculated as nitric acid) is, therefore, expressed by the following formula:

$$p = (T^1 - T + t)(A + a) - 0{\cdot}23n - 1{\cdot}6f \quad \text{(i)},$$

where,

$T$ = observed temperature before ignition,
$T^1$ = maximum temperature,
$t$ = correction for heat given up to surrounding air,
$A$ = weight of water in the calorimeter,
$a$ = *water-equivalent* of the apparatus, this being determined once and for all in a preliminary experiment,[1]
$n$ = milligrams of nitric acid formed,
$f$ = milligrams of iron in the igniting coil.

As regards this calculation, it may be pointed out that the various corrections indicated above compensate one another partly, so that, for

[1] The *water-equivalent* is the weight of water requiring the same amount of heat to raise its temperature 1° as the calorimetric apparatus (vessel, stirrer, thermometer, etc.). It is determined by an experiment with a substance of known heat of combustion (e.g., naphthalene, 9692; cane sugar, 3957; benzoic acid, 6330 cals.). The difference between the true calorific power of the substance and that calculated from the experimental results without taking account of the heat absorbed by the apparatus, divided by the rise of temperature, gives the required water-equivalent, if it is not thought desirable to allow for the corrections for the rigorously exact calculation; otherwise, $a$ is deduced from equation (i).

The water-equivalent may also be calculated theoretically (with less reliable results) by multiplying the weights of the different parts of the apparatus by the specific heats of the materials from which they are made and adding together the products thus obtained.

ordinary practical purposes, sufficiently exact results are obtained if the corrections are omitted. Under such circumstances the thermometric readings during the preliminary period and those after the maximum temperature has been passed, and also the titration, becomes useless, the only values required being those of the magnitudes in the expression,

$$p = (T^1 - T)(A + a) \quad \ldots\ldots \quad \text{(ii)},$$

which then gives the calorific power.

It must also be mentioned that, whilst in the bomb the water (hygroscopic water plus that formed by combustion of the hydrogen in the fuel) remains in the liquid state, in practice it passes off as vapour among the products of combustion; consequently, the calorific power calculated as above includes also the heat of condensation of the water, which in practice is not utilisable. In France the calorific power resulting from the above calculation, that is, presupposing the formation of liquid water (also called *gross calorific power*) is given, whereas in Germany, Austria, and elsewhere, the heat of condensation of the water is deducted, the assumption being made that the water remains as vapour (*net calorific power*). Taking 600 cals. as the heat of condensation of 1 gram of aqueous vapour, if H and M are the percentages of hydrogen and moisture in the fuel, the deduction to be made from the gross calorific power to obtain the net value is 6 (M + 9H). Where an elementary analysis is not made, a separate determination may be made of the total water evolved during the combustion (by burning a given weight of fuel in a tube and collecting the water in an absorption apparatus), or, as Mahler suggests, in practical cases mean values of H may be taken according to the quality of the fuel tested.

EXAMPLE: The experimental data obtained were as follows:

$A = 2200$ grams.
$a = 474$ ,,
$n = 0{\cdot}125$ ,,
$f = 0{\cdot}032$ ,,

Temperature observed:

| | | | | | |
|---|---|---|---|---|---|
| 0 minutes | 15·180° | | 7 minutes | 18·250° | |
| 1 ,, | 15·185 | | 8 ,, | 18·305 | (max.) |
| 2 ,, | 15·190 | | 9 ,, | 18·290 | |
| 3 ,, | 15·195 | | 10 ,, | 18·275 | |
| 4 ,, | 15·200 | | 11 ,, | 18·260 | |
| 5 ,, | 15·205 | (ignition) | 12 ,, | 18·245 | |
| 5½ ,, | 15·795 | | 13 ,, | 18·230 | |
| 6 ,, | 17·850 | | | | |

Hence $T^1 - T = 18{\cdot}305 - 15{\cdot}205 = 3{\cdot}100°$. The law of variation before ignition is given by

$$\frac{15{\cdot}205 - 15{\cdot}180}{5} = 0{\cdot}005°,$$

and that after the maximum is passed by

$$\frac{18{\cdot}305 - 18{\cdot}230}{5} = 0{\cdot}015°.$$

The correction to be made for the first half-minute after ignition is hence $-\frac{0{\cdot}005}{2} = -0{\cdot}0025°$; for the next half-minute it is $\frac{0{\cdot}015 - 0{\cdot}005}{2} = 0{\cdot}005$, and for each of the minutes, 6–7 and 7–8, it is 0·015. Hence

$$t = 2 \times 0{\cdot}015 + 0{\cdot}005 - 0{\cdot}0025 = 0{\cdot}0325.$$

Equation (i) then gives

$$p = (3{\cdot}100 + 0{\cdot}0325)(2200 + 474) - 0{\cdot}23 \times 125 - 1{\cdot}6 \times 3{\cdot}2 = 8296{\cdot}4 \text{ cals}$$

Calculating without corrections according to formula (ii),

$$p = 3{\cdot}1 \times (2200 + 474) = 8289{\cdot}4 \text{ cals.}$$

In this way the gross calorific power is found. If the fuel contains 3% of moisture and 4·5% of hydrogen, $6\ (3 + 9 \times 4{\cdot}5) = 261$ cals., must be subtracted from the results to obtain the net calorific power, which is therefore 8035·4 (corrected) or 8028·4 (uncorrected).

(*c*) HEMPEL'S CALORIMETRIC BOMB. This apparatus, which is simpler and cheaper than that of Mahler, consists (Fig. 36) of a cylindrical, thick-walled, cast-iron autoclave *A*, holding about 250 c.c. and coated inside with a thin layer of enamel. It has a screw lid *B*, which fits air-tight by means of an annular lead washer and has an aperture closable by a conical screw valve *a*. The lid carries two rods, one, *b*, connected directly with it, and the other, *c*, insulated by means of a rubber coating from the lid, through which it passes. Each rod terminates below in a platinum wire bent to a hook to support a capsule *d* of refractory earth, in which is placed the fuel compressed into cylindrical form in a mould. Between the two wires is fitted another very thin platinum wire, which penetrates into the cylinder of fuel and ignites the latter when heated to redness by a current.

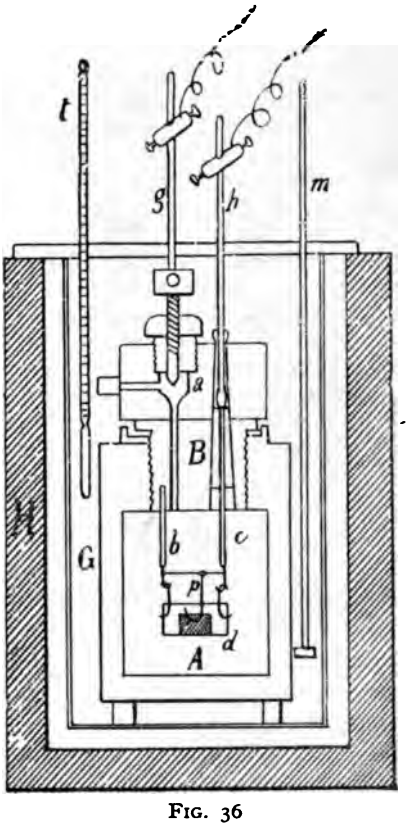


FIG. 36

The calorimeter is a cylindrical copper vessel *G* containing, besides the bomb, about 1 litre of water and placed in a wooden vessel *H* so that the distance between the walls is 2 cm. The whole is then closed by a cover, through which pass the two terminals, a thermometer *t* to read to 0·01° and a stirrer *m*.

The powdered fuel is pressed into a cylinder weighing about 1 gram into which the igniting wire is already pressed. It is weighed exactly and placed in the dish *d* and the bomb closed, oxygen being then passed in slowly until the pressure becomes about 15 atmos. The valve *a* is then closed and the bomb placed in a beaker of water to ascertain if it is air-tight; this being the case, it is dried and arranged in the calorimeter, the stirrer being put in motion and the thermometer read at intervals of a minute. After the temperature has remained constant for five minutes, the current is passed momentarily to cause ignition and the stirring continued and the periodic reading of the thermometer continued until the temperature passes

its maximum. The weight of water, plus the water-equivalent of the calorimeter (usually determined once for all by a preliminary measurement), multiplied by the rise of temperature, gives the heat generated. For a more exact calculation, the corrections indicated for the Mahler apparatus may be introduced.

Kroeker has modified the Hempel bomb by the addition to the lid of a second valve inserted in a platinum tube leading almost to the bottom of the bomb for the admittance, after the combustion, of a current of dry air into the bomb heated at 105° and the absorption of the expelled water vapour in a weighed calcium chloride solution. The amount of the total water thus determined is used in calculating the net calorific power.

## SPECIAL PART

## WOOD CHARCOAL

This is distinguished as *hard* or *soft*, according as it is made from hard or soft wood, and as *red* or *black* according to the degree of carbonisation to which it has been subjected. The black, composed principally of carbon, is in the more common use.

***

Charcoal contains usually 80–90% C, 1–3% H, 2–4% O, 6–10% $H_2O$ and 1–3% ash. As a rule, its calorific power lies between 6500 and 7500 cals.

## PEAT

This is a fuel of somewhat diverse origins and may, therefore, exhibit very varied aspect and composition. According to its origin, it is distinguished as *marsh*, *heath*, *meadow*, *forest*, and *marine* peat, and according to its appearance as mucous, spongy, herbaceous, earthy, compact, lignite-like, etc.

***

When freshly extracted, peat always contains a considerable quantity of water, which may vary from 50 to 90%, whilst, when air-dried, it still contains 10–30% of moisture. The percentage of ash varies widely and may be as much as 20–30% or even much more.

The best peats have compositions lying between the following limits, which refer to the dry product:

| | |
|---|---|
| Carbon | 50–60% |
| Hydrogen | 5–7% |
| Oxygen | 30–35% |
| Nitrogen | 1–2% |
| Ash | 5–10% |

The calorific value of a good peat usually varies between 3,000 and 4,000 calories, but a value of 5,000 cals. may be reached with dry peats poor in ash.

## LIGNITE

This exists in several varieties. Sometimes it has the aspect and colour of wood (*fossil wood*) and sometimes it is brown, friable and easy to break (*peaty, earthy lignite*) ; in some cases it consists of superposed layers (*schistose lignite*) and in others is compact and varying in colour from brown to shining black (*pitch coal*).

***

When newly won, lignites contain 20–60% of moisture, and when air-dried, 10–20%. The percentage of ash is very variable and, although it usually varies from 2 to 15%, it may also be much greater. The elementary composition referred to the fuel free from ash and moisture, generally varies between the following limits :

| | |
|---|---|
| Carbon | 55–75% |
| Hydrogen | 4–7% |
| Oxygen | 20–35% |
| Nitrogen | 0·5–2% |

In some lignites sulphur may be present in marked proportions. The calorific power of good lignites varies from 4,000 to 6,500 cals.

Table XXXVII (see p. 310) gives the analytical results for various lignites.

## COAL

Coal proper includes the *bituminous coals* and *anthracite* ; there is a gradual transition from the one to the other and no sharp delimitation. They constitute the most important industrial fuels. They are usually compact and black, the following types being distinguished : shining, black coal ; opaque, black ; cannel, of a velvety, blackish colour, with a conchoidal fracture ; fibrous coal ; and bituminous slates (boghead).

***

According to their chemical composition, coals are classified, after Gruner, in six categories, which differ in the quantity and quality of the coke they furnish and in their calorific powers. The normal limits for each of these classes are indicated in Table XXXVIII (p. 311), the data in which are referred to the pure fuel (free from moisture and ash).

## Table XXXVII

## Composition of Lignites

| Quality. | Chemical Composition. | | | | | | | Fixed Carbon. | Volatile Matters. | Calorific Power. | Author. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Carbon. | Hydrogen. | Oxygen. | Nitrogen. | Sulphur. | Ash. | Moisture. | | | | |
| *Italian* | | | | | | | | | | | |
| Leffe (Val Gandino, Bergamo) | 36·74–51·46 | 3·72–5·20 | 15·50–26·86 | 0·29–1·38 | 0·84–1.33 | 2·10–23·71 | 12·76–25·95 | 21·17–30·28 | 37·05–54·86 | 4060–5450[1] | Sestini & Camplani |
| Monterufoli (Volterra)[1] | 57·16–63·40 | 5·01–5·66 | 25·40–26·68 | | — | 5·54–11·15 | — | — | — | 5168–6478 | Capacci |
| Do. (do.) | — | — | — | — | 3·86 | 6·16 | 14·55 | 47·46 | 31·83 | 4690 | ,, |
| Murlo (Siena)[1] | 57·38–59·34 | 4·92–5·55 | 28–31·98 | | — | 3·13–9·70 | — | — | — | 5328 | ,, |
| Do. (do.) | — | — | — | — | 1·71 | 7·82 | 29·78 | 32·75 | 29·63 | 4415 | ,, |
| Montebamboli (Grosseto)[1] | 73·44 | 6·15 | 15·31 | | — | 5·10 | — | — | — | 7485 | ,, |
| Do. (do.)[1] | — | — | — | — | 2·34 | 6·00 | — | 60·00 | 34·00 | 6000 | ,, |
| Casteani (do.)[1] | 60·10 | 5·23 | 26·62 | | — | 8·05 | — | — | — | 5514 | ,, |
| Do. (do.)[1] | — | — | — | — | — | 0·55–7·32 | — | 53·68–61·85 | 37·60–39·00 | 6309 | ,, |
| S. Angelo e Morgnano (Spol.) | — | — | — | — | 0·87–3·03 | 2·23–22·81 | 36·09–42·59 | 17·85–23·75 | 19·72–38·50 | 1687–3900 | ,, |
| Bacu Abis (Gonnesa, Sardinia) | 57·95 | 4·61 | 8·93 | 4·26 | 7·28 | 10·87 | 6·63 | 39·18 | 43·32 | — | ,, |
| Do. (do.)[1] | 59·98–70·55 | 4·75–5·25 | 19·40–29·42 | | — | 4·80–5·85 | — | 46·15–55·15 | 42·05–48·00 | 5477–6440 | Galdi (from various authors) |
| *From other countries* | | | | | | | | | | | |
| Lausitz (Germany) (18 samples) | 50·41–55·87 | 3·76–5·23 | 18·00–26·31 | | 0·27–1·78 | 2·28–15·96 | 7·28–16·22 | — | — | 4550–5290 | Hinrichsen |
| Saxony, Thuringia, Anhalt (Germany) (44 samples) | 40·00–58·04 | 3·45–5·98 | 11·13–24·71 | | 0·87–6·03 | 6·94–25·08 | 8·47–23·15 | — | — | 3700–5670 | ,, |
| Southern Germany (10 samples) | 43·14–57·73 | 3·43–5·07 | 12·33–25·56 | | 0·44–6·27 | 4·29–19·62 | 9·15–14·36 | — | — | 3870–5380 | ,, |
| Bohemia (10 samples) | 50·32–63·97 | 3·98–5·26 | 5·60–19·06 | | 0·23–10·98 | 2·12–14·28 | 1·13–19·86 | — | — | 4780–6560 | ,, |
| Trifail (Styria) | 65·46 | 4·78 | 24·30 | | 1·47 | 4·75 | 0·71 | 46·95 | 47·59 | 6284 | Mahler |
| Salgo-Tarjan (Hungary) (3 samples) | 44·59–48·02 | 3·59–3·82 | 11·30–12·57 | 0·97–1·06 | 0·99–1·22 | 23·42–26·11 | 11·92–12·00 | — | — | 4165–4546 | Grittner |
| Petrozseny (Hungary) | 60·47 | 4·08 | 13·57 | 1·07 | 2·55 | 15·63 | 5·18 | — | — | 5623 | Gruner & Bousquet |
| Russia (6 samples) | 48·94–54·40 | 3·53–4·47 | 10·56–14·90 | | 1·62–4·88 | 15·71–19·25 | 7·95–12·37 | — | — | 4453–5140 | Hinrichsen |
| Vaugirard (France) | 59·80 | 4·51 | 25·80 | | 1·50 | 6·75 | 3·14 | 45·10 | 45·01 | 5536 | Mahler |
| Mouth of the Rhone (France) | 63·88 | 4·58 | 11·16 | | — | 13·43 | — | 41·10 | — | 5961 | Regnault |

[1] The data of these analyses refer to the dry substance; those of the others to the fuels as they stand.

TABLE XXXVIII

## Limits of Composition of Coals (Gruner)

(The values refer to dry, ashless coal)

| No. | Class. | Elementary percentage Composition. | | | Ratio $\frac{O+N}{H}$ | Percentage of | | Appearance and quality of the Coke. |
|---|---|---|---|---|---|---|---|---|
| | | C | H | O+N | | Coke (fixed carbon) | Volatile Matters. | |
| 1 | Dry long-flame coal (non-caking) | 75–80 | 5·5–4·5 | 19·5–15·5 | 4–3 | 50–60 | 50–40 | Pulverulent or only slightly coherent. |
| 2 | Fat, long-flame or gas coal | 80–85 | 5·8–5 | 14·2–10 | 3–2 | 60–68 | 40–32 | Caked but very porous. |
| 3 | Fat, caking or furnace coal | 84–89 | 5·5–5 | 11–5·5 | 2–1 | 68–74 | 32–26 | Caked, somewhat porous. |
| 4 | Fat, short-flame or caking coal | 88–91 | 5·5–4·5 | 6·5–4·5 | about 1 | 74–82 | 26–18 | Caked and compact. |
| 5 | Lean, short-flame or anthracitic coal | 90–93 | 4·5–4 | 5·5–3 | about 1 | 82–90 | 18–10 | Adherent or pulverulent. |
| 6 | Anthracite . . | 93–95 | 4–2 | 3 | about 1 | more than 90 | less than 10 | Pulverulent. |

The calorific power of coals, referred to the dry, ashless fuel, varies in general from 7600 to 8900 cals.

As regards the uses to which different coals are especially suited, long flame, non-caking coal (Class 1) is adapted to the manufacture of gas and particularly for reverberatory furnaces. Gas coal (Class 2) is preferred for making gas, since, in comparison with the preceding, it gives volatile matters richer in carbon and hence more illuminating, although in lower yield. Fat, caking or furnace coal is suitable for use in reverberatory furnaces and for making metallurgical coke ; for the latter purpose the short-flame caking coals are particularly adapted. Finally, the lean, short-flame or anthracitic coals and the anthracites, owing to their slow combustion and to the little smoke they give, are used for domestic purposes and for the heating of boilers, where a slow, quiet fire is required. Further, in consequence of the paucity of their volatile matters, the anthracites may be used directly in blast furnaces instead of coke.

For industrial purposes coal should not contain more than 2–3% of sulphur. The best coals contain 3–8% of ash and the proportion may be 12% in good coal, but coal with more than this is regarded as medium or bad. The moisture of unwashed coal should not exceed 3%.

Table XXXIX gives the analytical results for a number of bituminous coals and anthracites.

## TABLE XXXIX

### Compositions of Different Coals

| | | Chemical Composition. | | | | | | Coke. | Volatile Matter. | Calorific Power. | Author. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Carbon. | Hydrogen. | Oxygen. | Nitrogen. | Sulphur. | Ash. | Moisture. | | | | |
| | *British* | | | | | | | | | | | |
| Wales | Newport, Abercarn : caking coa | 84·77 | 4·98 | 4·66 | | 0·55 | 4·14 | 0·90 | — | — | — | From Gherardi |
| | Do. Western Valley : „ | 83·64 | 4·59 | 7·01 | 1·06 | 0·71 | 2·23 | 0·76 | — | — | 8058 | G. R. Thompson |
| | Do. Tillery : „ | 82·32 | 4·75 | 4·59 | | 1·03 | 6·59 | 0·72 | — | — | — | From Gherardi |
| | Do. Risca : „[1] | 83·25 | 4·96 | 3·40 | 1·65 | 0·79 | 5·95 | — | 68·9 | — | 7956 | „ |
| | Cardiff, Nixon's Navigation : Anthracitic[1] | 90·27 | 4·12 | 2·53 | 0·63 | 1·20 | 1·25 | — | 84·5 | — | — | „ |
| | Do. Ferndale : „ | 89·10 | 4·75 | 2·06 | 1·20 | 0·85 | 1·40 | 0·64 | 86·5 | — | 8131 | Gherardi |
| | Do. Cambrian Navigation : „[1] | 90·06 | 5·16 | 2·79 | 0·79 | 0·58 | 0·62 | — | 86·5 | — | — | Riley |
| | Do. Albion Merthyr : „ | 88·30 | 4·56 | 2·78 | 1·50 | 0·98 | 1·20 | 0·68 | 84·6 | — | 8080 | Gherardi |
| | Do. Penrikyber Navigation : „[1] | 90·41 | 4·82 | 1·71 | 0·96 | 0·71 | 1·39 | — | 89·1 | — | — | From Gherardi |
| | Do. Great Western Nav. : „ | 86·48 | 4·04 | 3·62 | 0·88 | 0·70 | 3·04 | 1·24 | 81·5 | — | 7755 | Treharne |
| | Do. Hill's Plymouth, Merthyr : „[1] | 89·49 | 4·00 | 3·78 | | 0·84 | 1·89 | — | — | — | — | From Gherardi |
| | Do. Oriental Merthyr : „ | 86·36 | 4·78 | 2·21 | 1·37 | 0·71 | 3·69 | 0·88 | — | — | 7964 | „ |
| | Do. Ynysfaio Merthyr : „ | 84·20 | 3·90 | 2·49 | 1·17 | 0·96 | 6·65 | 0·63 | 85·2 | — | — | „ |
| | Do. Lewys Merthyr : „ | 86·40 | 4·05 | 1·97 | 1·10 | 0·96 | 4·57 | 0·95 | 84·7 | — | 7956 | Gherardi |
| | Do. Naval Merthyr : „ | 88·83 | 4·63 | 2·02 | 1·10 | 0·50 | 2·60 | 0·32 | 85·7 | — | 8080 | „ |
| | Do. Standard Merthyr : „ | 87·21 | 4·11 | 1·75 | 1·60 | 1·05 | 3·68 | 0·60 | — | — | — | From Gherardi |
| | Swansea, Peacock : Anthracitic[1 2] | 90·61 | 3·77 | 2·32 | | 0·98 | 2·28 | — | 91·52 | 6·20 | 8589 | Seyler |
| | Do. Abercrave : „[1 2] | 91·25 | 3·60 | 2·32 | | 0·83 | 2·00 | — | 92·04 | 5·96 | 8541 | Morgan & Seyler |
| | Do. Tirydail : „[1 2] | 91·60 | 3·61 | 3·25 | | 0·44 | 1·10 | — | 93·60 | 5·30 | — | „ „ |
| | Do. Bonville's Court „[1] | 94·18 | 2·99 | 0·50 | 0·76 | 0·59 | 0·98 | — | — | — | — | Frankland |
| | Newcastle, Pelaw Main : Gas coal | 82·58 | 4·42 | 6·64 | 0·85 | 0·81 | 3·47 | 1·23 | 71·6 | 28·4 | — | From Gherardi |
| | Do. Newpelton : „ | 84·93 | 5·13 | 4·92 | 1·53 | 1·14 | 1·48 | 0·87 | 69·6 | 30·4 | — | „ |
| | Do. Lambton : „ | 84·06 | 5·11 | 6·34 | 0·75 | 0·82 | 1·36 | 1·56 | 67·8 | 32·2 | — | „ |
| | Do. Boldon : „ | 82·36 | 5·11 | 6·56 | 1·05 | 0·86 | 2·04 | 2·02 | 66·7 | 33·3 | — | „ |
| | Do. Holmside : „ | — | — | — | — | 1·53 | 0·95 | 0·90 | 68·3 | 31·7 | — | „ |
| | Do. Bothal : Engine coal[1] | 80·90 | 5·33 | 9·64 | 0·96 | 0·77 | 2·40 | — | 62·3 | 37·7 | 7955 | „ |
| | Do. Rawensworth : „ | 75·05 | 4·91 | 7·87 | 1·80 | 1·04 | 1·86 | 7·47 | 57·5 | 42·5 | 7356 | „ |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Lancashire, Wigan : Cannel coal [1] | 79·23 | 6·08 | 7·24 | 1·18 | 1·43 | 4·84 | — | 60·3 | 39·7 | — | Playfair and de la Beche |
| Do. Rushy Park : Steam coal [1] | 77·65 | 5·33 | 10·91 | 0·50 | 1·73 | 3·88 | — | 59·4 | 40·6 | — | From Gherardi |
| Yorkshire, Denaby Main : Engine coal [1] | 85·71 | 3·49 | 6·50 | 1·89 | 0·30 | 2·11 | — | 56·7 | 43·3 | — | ,, |
| Staffordshire, Rowhurst : Gas coal | 68·90 | 5·17 | 12·18 | 1·68 | 0·51 | 7·04 | 4·52 | 63·5 | 36·5 | 6825 | ,, |
| Bristol, Timsbury : Gas coal [2] | — | — | — | — | 1·10 | 7·68 | 0·54 | 63·0 | 27·7 | — | ,, |
| Scotland, Wilson Navigation : Engine coal [1] | 86·64 | 4·99 | 4·06 | 1·26 | 0·84 | 2·21 | — | 70·5 | 29·5 | 7706 | ,, |
| Do. Hamilton Splint : Gas coal | 71·84 | 5·24 | 8·51 | 1·39 | 0·52 | 2·95 | 9·55 | 54·5 | 45·5 | 7247 | ,, |
| Do. Bent : Cannel coal [2] | — | — | — | — | 0·87 | 3·22 | 6·25 | 53·8 | 36·2 | — | Hislop |
| Do. Ayrshire : Main, Steam coal [1] | 79·82 | 5·82 | 11·31 | 0·94 | 0·86 | 1·25 | — | 49·3 | 50·7 | — | From Gherardi |
| Do. Lesmahagow : Cannel coal [1] | 73·44 | 7·62 | 11·77 | | 1·14 | 6·03 | — | 43·3 | — | — | ,, |
| Do. Edinburgh : Boghead [1] | 63·10 | 8·91 | 7·25 | | 0·96 | 19·78 | — | — | — | — | ,, |
| *German and Austrian* | | | | | | | | | | | |
| Upper Silesia (128 samples) | 55·46–81·50 | 3·82–5·38 | 5·19–15·23 | | 0·29–2·80 | 1·77–23·68 | 0·70–7·99 | — | — | 5550–7730 | Hinrichsen |
| Lower Silesia (24 samples) | 61·89–79·26 | 0·56–4·86 | 1·74–12·33 | | 0·74–1·67 | 6·13–33·85 | 0·81–4·93 | — | — | 5120–7170 | ,, |
| Rhine Provinces and Westphalia (38 samples) | 58·82–84·24 | 3·83–5·48 | 2·13–11·25 | | 0·71–4·77 | 3·04–23·52 | 0·42–7·04 | — | — | 6590–8000 | ,, |
| Saar Basin (5 samples) | 63·00–76·97 | 4·00–4·97 | 6·57–10·12 | | 0·79–1·12 | 9·36–24·12 | 1·01–4·56 | — | — | 6000–7510 | ,, |
| Saxony (7 samples) | 53·04–76·62 | 3·13–4·91 | 7·75–10·80 | | 1·03–2·24 | 5·25–31·04 | 2·65–6·23 | — | — | 4950–7270 | ,, |
| Bohemia (6 samples) | 64·09–70·63 | 3·65–4·83 | 8·42–17·24 | | 0·92–1·03 | 2·58–10·98 | 5·90–10·65 | — | — | 6026–6633 | Foullon |
| *French* | | | | | | | | | | | |
| Anzin (Nord) : Caking coal [2] | 83·75 | 4·39 | 5·76 | | — | 5·00 | 1·10 | 73·70 | 20·20 | 8051 | Mahler |
| Lens (Pas de Calais) : Caking coal [2] | 87·74 | 4·68 | 5·03 | | 0·86 | 1·55 | 1·00 | 78·45 | 19·00 | 8614 | ,, |
| Do. do. Gas coal [2] | 83·73 | 5·22 | 7·00 | | — | 3·00 | 1·05 | 66·40 | 29·55 | 8395 | ,, |
| Firminy (St. Etienne) : Gas coal [2] | 81·27 | 5·31 | 8·59 | | — | 3·60 | 1·23 | 64·70 | 30·47 | 8161 | ,, |
| Grand' Combe (Gard) : Coke coal [2] | 87·16 | 4·27 | 4·16 | | — | 3·80 | 0·61 | 82·80 | 12·79 | 8371 | ,, |
| Blanzy (Côte d'Or) : Non-caking, long-flame coal [2] | 74·73 | 5·17 | 11·75 | | 1·28 | 4·85 | 3·50 | 55·55 | 36·10 | 7408 | ,, |
| Creuzot (Côte d'Or) : Anthracitic coal [2] | 89·39 | 3·66 | 3·70 | | — | 1·45 | 1·80 | 86·65 | 10·10 | 8404 | ,, |
| Commentry (Allier) : Gas coal [2] | 80·18 | 5·25 | 8·17 | | 0·59 | 3·40 | 3·00 | 56·20 | 37·40 | 7870 | ,, |
| Isère : Anthracite [1] | 94·00 | 1·49 | 0·85 | | — | 3·66 | — | — | — | — | Jacquelin |
| *Belgian.* | | | | | | | | | | | |
| Grand Buisson (Mons) : Caking coal [1] | 83·40 | 5·40 | 7·76 | | — | 3·44 | — | — | — | — | De Marsilly |
| Belle Vue (Mons) : Short-flame, caking coal [1] | 86·38 | 4·48 | 6·09 | | — | 3·05 | — | — | — | — | ,, |
| Saint Martin (Charleroi) : ,, ,, [1] | 86·23 | 4·62 | 5·81 | | — | 3·34 | — | — | — | — | ,, |
| Beaulet (Charleroi) : Anthracitic coal [1] | 90·89 | 3·65 | 3·98 | | — | 1·48 | — | — | — | — | ,, |

[1] In these analyses the numbers refer to the dry fuel; in the others to the fuels as they stand.
[2] In these analyses the numbers in the *Coke* column represent fixed carbon (coke minus ash).

TABLE XXXIX (*continued*)

## Compositions of Different Coals

| | Chemical Composition. | | | | | | | Coke. | Volatile Matter. | Calorific Power. | Author. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Carbon. | Hydrogen. | Oxygen. | Nitrogen. | Sulphur. | Ash. | Moisture. | | | | |
| *Russian* | | | | | | | | | | | |
| Various (16 samples) | 51·42–70·54 | 3·54–4·81 | 10·18–15·43 | | 0·72–2·37 | 4·26–27·48 | 4·71–9·63 | — | — | 4800–6490 | Hinrichsen |
| Koutschenkowo (S. Russia): Caking coal | 81·52 | 4·81 | 12·94 | | 0·74 | 0·73 | — | — | — | — | Alexejew |
| *American* | | | | | | | | | | | |
| Pennsylvania (3 samples)[1] | 76·60–80·10 | 4·35–4·61 | 8·41–10·22 | 1·05–1·10 | 0·65–1·30 | 5·38–6·35 | — | — | — | — | Fischer. |
| Do. (2 samples)[2] | — | — | — | | 0·97–0·98 | 5·87–7·24 | 0·71–1·47 | 63·66–76·83 | 16·59–27·63 | 7875–8296 | U.S. Geol. Survey |
| Southern Virginia (3 samples)[2] | — | — | — | | 0·46–1·65 | 3·14–4·63 | 0·47–0·80 | 62·33–81·59 | 14·80–32·24 | 8167–8447 | ,, |
| Illinois (2 samples)[2] | — | — | — | | 0·48–0·95 | 5·68–8·58 | 4·00–7·67 | 57·69–58·56 | 28·86–28·96 | 6958–7056 | ,, |
| Pennsylvania: Anthracite[2] | — | — | — | | 0·46–1·03 | 4·38–11·23 | 1·30–4·12 | 80·87–87·98 | 3·08–8·10 | — | Penns.Geol.Surv. |
| Do. do.[2] | 86·45 | 2·00 | 2·20 | | — | 5·90 | 3·45 | 87·93 | 2·72 | 7484 | Mahler |
| *Asiatic* | | | | | | | | | | | |
| Japan (6 samples)[2] | — | — | — | | 0·23–0·53 | 1·82–6·86 | 1·42–2·45 | 45·87–53·42 | 43·18–48·71 | — | — |
| China (4 samples) | — | — | — | | 0·34–4·34 | 8·90–19·80 | 0·60–4·70 | 57·85–76·80 | 8·30–31·68 | 6809–7533 | — |
| *Italian Anthracites* | | | | | | | | | | | |
| Ollano, Bormida (Liguria)[2] | — | — | — | | — | 25·43 | 6·78 | 65·30 | 2·49 | 5300 | Mattirolo |
| Osiglia (Liguria)[2] | — | — | — | | — | 12·43 | 4·01 | 79·75 | 3·81 | 6500 | ,, |
| Min. Prailet, La Thuile (Val d'Aosta)[2] | — | — | — | | — | 19·25 | 5·98 | 71·38 | 3·39 | 5780 | ,, |

[1] In these analyses the numbers refer to the dry fuel; in the others to the fuels as they stand.
[2] In these analyses the numbers in the *Coke* column represent fixed carbon (coke minus ash).

## COKE

Ordinary heating coke, obtained as a secondary product in the manufacture of illuminating gas from long-flame bituminous coal, forms more or less opaque, highly porous lumps of a grey colour. Metallurgical coke, which is obtained from a fat, short-flame coal, is resistant, sonorous and pale grey with metallic lustre. In every case, coke consists, apart from ash, essentially of carbon.

***

Unwashed coke should contain only 1–2% of moisture; if washed and air-dried it may contain as much as 5–6%. With certain cokes the ash may amount to 20%, but good samples usually contain 4–10%.

Further, coke usually contains 83–90% C, 0·3–2% H, 2–6% O and 1–2% N; the proportion of sulphur may reach 2·5%, but for metallurgical coke the usual requirement is that it shall not exceed 1%. With cokes not excessively rich in ash, the calorific power varies from 7000 to 8000 calories.

In England it is required that a good metallurgical coke should not contain more than 4% of water, 8% of ash and 0·5% of sulphur, and that its calorific power should be about 8000 cals.

## AGGLOMERATED FUELS

### (Briquettes)

These vary in quality with the coal and agglutinating material used in their manufacture. Bituminous coal is the more commonly employed and pitch is mostly taken to act as cohesive, although many other materials have been proposed.

Briquettes are usually brick-shaped, but cylinders, sometimes perforated to facilitate access of air, and ovoid forms are also made.

With these fuels, in addition to the determinations given under the heading "General methods," it is important to ascertain the *cohesion or compactness*. This may be done with a special apparatus, or by a crushing test normal to the largest face (with brick-shaped briquettes).

In some cases also the *resistance to heat* is tested, in order to find out if the briquettes soften when kept for a certain time at a definite temperature (e.g., 6 hours at 60°).

The *determination of the pitch* used as agglutinant may be carried out approximately by extraction in a Soxhlet apparatus with carbon disulphide until the latter ceases to become coloured (this usually requires at least 10 hours), evaporating the carbon disulphide and weighing the residue after drying at 120°. In this way, however, only 50–60% of the pitch actually used is extracted.

***

The conditions to be satisfied by briquettes vary with the quality and with the uses to be made of them. In general it is required that they should be homo-

geneous, not too brittle, almost odourless and non-hygroscopic, and that they do not break up in the furnace or give too much smoke when burning.

As regards briquettes of bituminous coal, the amount of pitch used varies between 5 and 10% and is commonly about 8%. The moisture should not exceed 5% and the ash, which in good qualities is often not more than 7%, should not be more than 9–10%; the volatile matters vary from 14 to 24%, but are ordinarily about 16%. Good bituminous briquettes should not contain more than 1·2% of sulphur, and their calorific power should be about equal to that of the good coal from which they are made and in general should not be below 7500 cals.

CHAPTER VII

# COAL TAR

## AND ITS PRODUCTS

During the dry distillation of coal, as in the manufacture of illuminating gas and in the preparation of coke, *crude tar* is collected as a secondary product. When subjected to further treatment this gives, on distillation, *tar oils*, these being distinguished according to the temperature at which they are collected, as *light*, *medium*, *heavy* and *anthracene oils*. The residue from the distillation is *pitch*. From the light oils are obtained, by further distillations, *benzene* (benzole) and the *toluenes* (toluoles), which are used in the dye and explosive industries and as solvents. The medium, heavy and anthracene oils yield other products of industrial importance, such as *naphthalene*, *anthracene*, *carbolic acid*, *pyridine bases* and *impregnating oils*. All of these products are considered separately in succeeding paragraphs, the tests commonly made in each case being indicated.

**Sampling.**—With very viscous liquids, such as crude tar and heavy and anthracene oils, it is not easy to obtain a sample exactly representing the mean composition of the whole mass. To take such a sample from the vessel or tank containing the material, use is made of a metallic dipping cylinder 4–5 cm. wide and closed at the bottom by a plug which is raised or lowered by means of an iron wire passing through the cylinder itself. The cylinder is filled several times and all the samples mixed so as to obtain as representative a sample as possible. With a non-viscous liquid, however, it is sufficient to mix the mass before extracting the sample.

With solid products such as naphthalene and anthracene, the mass must be examined to see if it is all of the same appearance, and samples should be drawn from different parts and mixed before analysis.

## CRUDE TAR

This is a dense, black, oily liquid with a characteristic odour due to the presence of aromatic hydrocarbons, phenols, naphthalene and pyridine bases. When it is to be distilled, the tests made are 1–4 (below), but if it is to be used as a fuel, the ash content and the calorific power are determined as with mineral oils (*q.v.*).

**1. Determination of the Water.**—Since tar exhibits a tendency to allow the water present to separate, either the sample should be taken immediately after the whole mass has been mixed, or the separated water

should be removed with a pipette and measured, the value given by the subsequent determination being suitably increased.

In a glass or copper distillation flask, a weighed quantity of 100 grams of the well-mixed sample is distilled with 50 c.c. of benzene (90% and 50%) through a condenser. The distillation is carried up to 190° in about half an hour, the distillate being collected in a graduated cylinder and the volume of the aqueous layer read off. Industrially, the water is determined directly during the distillation test and is collected with the light oils, from which it separates on standing, so that it may be easily measured.

**2. Determination of the Specific Gravity.**—The tar is first completely freed from water. To this end it is left for 24 hours in a closed vessel in a bath of water heated to a temperature not higher than 50°, being shaken from time to time to facilitate the rising of the drops of water and air bubbles. When the layer of water is thoroughly separated, it is decanted or siphoned off and the specific gravity of the residual tar determined at 15° C. With a fairly mobile tar, an ordinary densimeter or picnometer is used, but with very dense tar either a picnometer for solids, with a wide mouth and a ground stopper surmounted by a tube with a mark on it, or an ordinary weighing bottle with a rill in the stopper [1] may be used.

**3. Determination of the Free Carbon.**—According to Köhler's method,[2] 10 grams of the tar are boiled with 25 c.c. of acetic acid and 25 c.c. of toluene in a conical flask with a reflux apparatus and the hot liquid filtered through two filter-papers reduced to equal weight and placed one inside the other. The residue on the filter is washed with hot toluene until the latter passes through colourless, the two filters being then separated and dried at about 120° until of constant weight. The difference in weight between the two filters gives the free carbon.

From the content of free carbon ($c$) thus obtained, the yield of a tar in pitch of a definite hardness may be determined—knowing the proportion, $k$, of free carbon in the pitch—by the formula $x = \frac{100\,c}{k}$.

Assuming that, for a good pitch of medium hardness, $k$ is 28%, a tar containing $c$% of free carbon will give $x = (100c \div 28)$% of such pitch.

**4. Fractional Distillation.**—Fractional distillation of tar presents difficulties on account of the bumping, which is due mainly to the presence of water. It is, therefore, necessary first to dehydrate the tar as completely as possible in the manner indicated above, then to distil from a flask not more than half full and to heat with great care until all the residual water is eliminated. The apparatus used for the distillation of mineral oils may be employed (*see* Chapter VIII). It is also advantageous to pass through the boiling liquid a gentle current of air by means of a capillary tube dipping into the liquid, the boiling being thus rendered more even. During the initial stages of the distillation use is made of a condenser, which is removed when the distillate tends to solidify in the tube. As regards the limits of temperature, four successive fractions are usually collected:

[1] *See* Lunge: *Coal Tar and Ammonia*, 1916, Part I, p. 520.
[2] *Dingler's Polyt. Journ.*, 1888, 270, p. 233.

(1) Up to 170°—light oils.

(2) From 170° to 230°—middle or carbolic oils.

(3) From 230 to 270°—heavy or creosote oils.

(4) Above 270° (distilled without thermometer)—green or anthracene oils.

The distillation is discontinued when, almost all the tar being distilled, the drops passing over become intensely red. The residue in the retort, representing the pitch, is weighed.

Industrially the distillation test is carried out on larger quantities (0·5 to 5 kilos) in a metallic vessel, so that results in greater accord with those of the works may be obtained.[1]

***

The specific gravity of coal tar (dry) usually varies from 1·100 to 1·280, but in exceptional cases may be below 1. The composition of the tar varies according to the character of the coal yielding it and to the mode of heating (whether in vertical or horizontal retorts), and similar variation is shown by the yield of distillation products. Tar contains 10–35% of free carbon and the quantity of water permissible in it when sold to the distilleries is 4–5%.

## CRUDE LIGHT TAR OILS

Analysis of these products includes the following determinations :

**1. Determination of the Specific Gravity.**—By means of a hydrometer or Westphal balance at 15° C.

**2. Distillation.**—100 c.c. are fractionally distilled from a glass or, better, copper vessel of 150 c.c. capacity, furnished with a thermometer and connected with a condenser. The portion passing over up to 120° is the crude benzole (with toluole, etc.) and that between 120° and 170°, the naphtha (*solvent naphtha*) ; the residue is regarded as middle oils. The distillates may be tested by the reactions for detecting the presence of any light petroleum oils (benzine) or oil of turpentine (*see* later : Benzole, 3, *c*, and also Oil of Turpentine, Vol. II).

**3. Determination of the Phenols.**—The fractions obtained from the preceding distillation are reunited, the containing vessels being rinsed out with xylene and the whole introduced into a 500 c.c. graduated cylinder with a ground stopper and repeatedly shaken with 100 c.c. of caustic soda solution (D 1·2). After being left at rest for some time, the volume of soda solution underneath is read, the increase in its volume giving the percentage of phenols by volume.

For a more exact determination the alkaline layer is collected and evaporated on a water-bath until addition of water no longer produces turbidity. When cold, the liquid is acidified with hydrochloric acid and treated with sodium chloride, the layer of phenols which separates being measured.

**4. Determination of the Bases.**—The oil freed from phenols by the treatment just described is repeatedly shaken with 30 c.c. of 20% sulphuric

[1] Lunge : *Technical Methods of Chemical Analysis* (London, 1911), Vol. II, p. 763.

acid in a graduated cylinder, the increase in volume of the lower layer giving the percentage by volume of the bases. These may also be determined directly by collecting the acid liquid, carefully adding to it a large excess of caustic soda solution (D 1·40), and measuring the bases which separate.

***

The specific gravity of the light oils usually lies between 0·900 and 0·950. Normal oils give about 90% of distillate up to 200° and have the specific gravity 0·930; they contain 5–15% of phenols and 1–3% of bases.

## MIDDLE AND HEAVY TAR OILS

With these the following determinations are made:

**1. Determination of the Specific Gravity.**—As with light oils.

**2. Distillation.**—This is carried out either with the product as it stands, which is distilled from a flask with a long side-tube but no condenser (to prevent crystallisation of naphthalene), or with the product free from naphthalene, or with that free also from phenols and bases, resulting from determinations 3 and 4.

**3. Determination of the Crude Naphthalene.**—From 0·5 to 2 kilos of the oil is left for 24 hours at 15° and then cooled if necessary to cause the naphthalene to crystallise, this being pumped off on a cloth or paper filter, pressed in a press until all the oily part is removed and weighed. This represents the crude naphthalene, of which the melting and boiling points may be determined.

**4. Other Determinations.**—The oil free from naphthalene is treated with caustic soda to determine the phenols, and with dilute sulphuric acid to determine the pyridine bases, as with the light oils (3 and 4).

***

A *good middle oil* has a specific gravity not less than 1; at least 90% of it distil below 260°, and it contains not less than 30% of crude naphthalene (b.p. 210–220°). The naphthalene-free oil has the specific gravity 0·99–1·01, and contains 25–35% of phenols (about one-third of this being carbolic acid) and about 5% of bases.

The *heavy oils* have a mean specific gravity 1·04 and distil between 200° and 300°; they contain mainly naphthalene and other solid hydrocarbons. together with 8–10% of phenols (principally cresols and higher homologues) and about 6% of pyridine bases.

## ANTHRACENE OILS

The analysis of anthracene oils includes, besides determinations of the specific gravity and of the behaviour on distillation—which are carried out as with the middle oils—only the determination of the anthracene, which is effected by transforming it into anthraquinone by means of chromic acid (*see later*: Anthracene, 1).

***

*Anthracene oils* have the specific gravity about 1·1 and boil between 280° and 400°; they are solid at the ordinary temperature and fluid at 60° and contain 2·5–3·5% of pure anthracene and about 6% of higher phenols.

## PITCH

This exists in the three forms, *soft*, *hard* and *extra hard*, and the tests made are for the purpose of ascertaining to which class the sample belongs and hence to what uses it may well be put.

**1 Determination of the Specific Gravity.**—With the picnometer in the ordinary way for solids; very hard pitches should first be powdered.

**2. Determination of the Free Carbon.**—As with tar (*see* Crude Tar, 3, p. 318).

**3. Determination of the Ash.**—2 or 3 grams of the pitch are burnt in a porcelain crucible in a muffle and the residue weighed.

**4. Determination of the Volatile Matter and Coke.**—As with fuels (*q.v.*). It is important to note the appearance of the coke—whether swollen, compact or coked.

**5. Softening and Melting Temperatures.**—These serve better than other tests to indicate the degree of purity of the pitch. In a beaker of water containing about half a litre of water is suspended a cube of the pitch of about 13 mm. side or a disc 4–5 mm. thick at the end of an iron wire, the pitch being 5 cm. from the bottom. A thermometer is immersed with the bulb at the same depth as the pitch and the temperature of the water raised 5° per minute. From time to time the pitch is withdrawn to ascertain how it behaves when pressed between the fingers. The *temperature of incipient softening* is taken as the lowest at which the pitch can be twisted without breaking, while the *temperature of softening* is that at which it can be moulded between the fingers without force and the *melting point* as that at which it begins to drop.

**6. Distinction between Tar Pitch, other Pitches and Natural Asphalt.**—The characters of these products are as follows:

| Coal-tar Pitch. | Vegetable Pitch (Black or Marine Pitch). | Petroleum Pitch. | Stearine Pitch. | Natural Bitumen. |
|---|---|---|---|---|
| Black, more or less stiff, with an odour of tar. | Black, with an odour recalling that of vegetable tar. | Black, almost odourless. | Black, odour of fatty substances. | Blackish, usually solid and hard, sometimes soft. |
| Slightly soluble in alcohol, the solution giving the reactions for phenols; very slightly soluble in light petroleum. | Very soluble in alcohol, giving a brown solution containing resinous matters and giving the reactions for phenols. It colours potash solution brown. | Almost completely insoluble in petroleum ether. | Insoluble in alcohol and partially soluble in petroleum ether. | Insoluble in alcohol; does not give the reactions for phenols. |
| The distillate has an alkaline reaction. | The distillate has an acid reaction. | In general has no saponification number. | Has a saponification number and an acid number. Evolves acrolein when heated. | |

The specific gravity of soft pitches is usually 1·250–1·265, that of hard 1·275–1·280, and that of very hard 1·275–1·280. For pitch from gas tar, the carbon content is rarely less than 25–30%, and for that from vertical retorts or blast-furnaces, 5–7%. The ash content is less than 0·5% for gas pitch and more than 1% (6–10%) for that from blast-furnaces. The yield of coke varies from 30 to 60%, and the coke has a more or less porous appearance according to the type of pitch from which it is derived (very porous with the very hard pitches, less so with the others).

As regards the temperatures of softening and fusion, the following limits may be taken for different types of pitch:

*Soft:* Softens at 40°, melts at 50–60°.

*Hard:* Softens at 60°, melts at 70–80°.

*Very hard:* Softens at 80–85°, melts at 90–120°.

A good pitch for making briquettes should, according to Spilker [1] have the following properties: not more than 0·5% of ash; softening point between 60° and 75°; solubility in aniline, 70–75%, and in carbon disulphide, not less than 70%; yield of coke, 45%; appearance of coke, caking and not too much swollen.

## IMPREGNATING OILS

These are usually creosote oils or anthracene oils, freed more or less completely from crystallisable substances, and are used for the impregnation of wood, especially railway sleepers and telegraph poles, with the object of preserving it.

In general they are brownish red or blackish liquids, more or less fluorescent, somewhat viscous, and with a more or less marked odour of the products of tar distillation.

The principal tests to be made are:

**1. Determination of the Specific Gravity.**—By means of a hydrometer or Westphal balance at 15° C.

In some cases measurements are made at higher temperatures, e.g., at 25, 45, 50° C.; the temperature used must be indicated in the report.

**2. Distillation.**—This is carried out in a tubulated retort of about 300 c.c. capacity, furnished with a thermometer. The retort is charged with 100 c.c. of the liquid and the thermometer bulb arranged at about 2 cm. from the liquid, which is heated so that 120 drops per minute pass over; the different fractions are measured.

**3. Determination of the Phenols and the Naphthalene.**—The fractions obtained as under 2 are reunited in a graduated cylinder, shaken repeatedly with 100 c.c. of caustic soda solution (D 1·15) saturated with sodium chloride and then left to settle; the increase in volume of the soda solution gives the percentage of phenols. In the supernatant oily layer the naphthalene is determined by cooling (to 15°) in the manner indicated for middle oils.

**4. Test for the Presence of Solid Substances.**—20 c.c. should remain liquid when heated to 40° and when shaken with 20 c.c. of pure benzene: when filtered through paper, the solution thus obtained should not leave a brown mark on the filter.

[1] Lunge: *Coal-Tar and Ammonia* (London, 1916), p. 542.

**5. Other Determinations.**—The temperature of inflammability and the viscosity may also be required; these are ascertained as with heavy mineral oils (*see* these: Chapter VIII).

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The composition of impregnating oils varies according to the conditions of the contract. Thus, a specific gravity of 1·03–1·10 or of 1·05 at 50° is required: a content of 5–30% of naphthalene; a content in phenols of 5–10%, and various boiling points.[1]

## BENZOLES

Commercial benzoles from the tar industry are mixtures in varying proportions of benzene, toluene and xylenes, and contain also ethylbenzene, trimethylbenzenes and other homologues of benzene. The separate pure hydrocarbons are obtained by further and complicated rectifications.

The rectified benzoles are colourless, limpid liquids with a characteristic, pleasant odour; any turbidity indicates presence of water.

The tests and determinations to be made are:

**1. Determination of the Specific Gravity.**—By the Westphal balance, densimeter or picnometer.

**2. Distillation.** — This test, which serves to characterise commercial benzoles, may be carried out in an ordinary distillation flask, similar to that used for light mineral oils. Industrially, however, the detailed instructions given by Kraemer and Spilker[2] are followed, so that comparable results may be obtained.

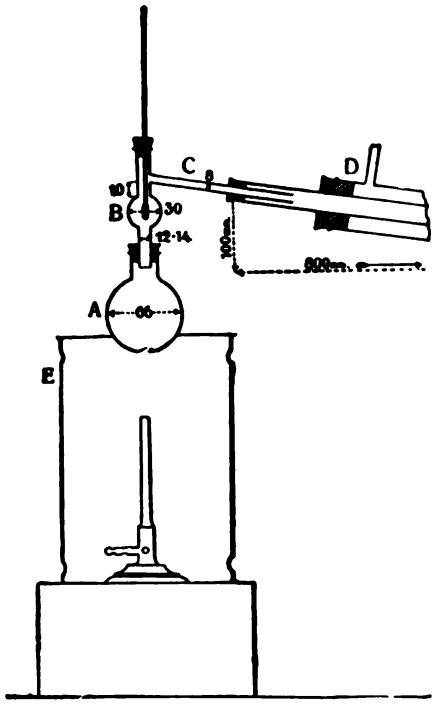


FIG. 37

The distillation apparatus used is represented in Fig. 37 and consists of a copper vessel *A*, 0·6–0·7 mm. thick, about 150 c.c. in capacity and of the dimensions indicated. To the mouth of the vessel is fitted a dephlegmator *B*, 14 mm. wide and 150 mm. long, furnished with a bulb and with a side-tube, 8 mm. in diameter, fixed almost at right angles. A thermometer, reading to 0·1° or 0·05° (for commercial benzoles) is introduced so that its bulb is in the centre of the bulb.

[1] For greater details, see Lunge: *Coal-Tar and Ammonia* (London, 1916), p. 695; Allen: *Commercial Organic Analysis*, 4th edit., 1910, Vol. III, p. 368.

[2] Muspratt: *Chemie*, 4th edit., 1905, Vol. VIII, p. 34.

The copper vessel rests on a circular aperture, 50 mm. in diameter, in a piece of asbestos card *E*, supported on an oven closed at the sides and provided at its upper part with four 10 mm. holes to allow of the circulation of the air. The heating is effected by a Bunsen burner of 7 mm. aperture.

The lateral tube of the dephlegmator is connected with a condenser *D*, 800 mm. long, inclined so that the top end is 100 mm. higher than the free end.

With this apparatus 100 c.c. of the liquid are distilled in such a manner that 5 c.c. distil over per minute (2 drops per second), fractions passing over at different temperatures (up to 100°, 120°, 145°, 160°, 175°, 190°, according to the different types of benzole) being collected in a graduated cylinder and measured.

For exact determinations it is necessary to take account of the atmospheric pressure, bearing in mind that for pressures between 720 and 780 mm. the percentages given by the distillation should be diminished by 0·033 for 90% benzoles and by 0·077 for 50% benzoles for each millimetre of pressure below the normal pressure of 760 mm. and increased by the same amounts for each millimetre above 760 mm.

**3. Determinations of the Separate Hydrocarbons.**—To separate and estimate approximately the different hydrocarbons contained in commercial benzole, the latter must be fractionally distilled in a manner rather different from that just described, a moderately large amount of substance being treated in an apparatus furnished with an efficient dephlegmator. Use is generally made of a copper vessel of the form and dimensions indicated (in millimetres) in Fig. 38, a six-bulb Le Bel-Henninger fractionator, 60 cm. long, being fitted to it. The fractionator is provided with a thermometer and joined to a condenser, and 1 kilo of the product is distilled at the same rate as in 2 (above), the different fractions being collected in tared receivers, which are subsequently reweighed.

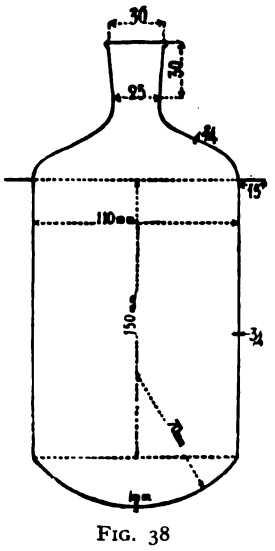

FIG. 38

The separation of the different hydrocarbons may be effected by further fractional distillations, regard being paid to the boiling points, which are as follows: benzole, 80–81°; toluole, 110–111°; xyloles, 138–142° (*o*-xylene, 142°; *m*-xylene, 139–140°; *p*-xylene, 138–139°); ethylbenzene, 137°; trimethylbenzenes, 163–175°.

The fractionation of the different commercial products is carried out on the basis of the following temperature limits:

| | Benzole (50% and 90%): | Pure commercial Benzole. | Toluole. | Xyloles. |
|---|---|---|---|---|
| First fraction | up to 79° | up to 79° | | |
| Benzole | 79–85 | 79–81 | up to 109° | up to 135° |
| Intermediate fraction | 85–105 | | | |
| Toluole | 105–115 | | 109–110·5 | |
| Xyloles | residue | residue | | 135–145 |
| Higher homologues, etc. | | | residue | residue |

The separation of the three xyloles (xylenes), which is usually not required, cannot be effected by means of fractional distillation, their boiling points being too similar. The respective quantities may, however, be determined approximately by regarding the distillate between 135° and 137° as *p*-xylene, that between 137° and 140° as *m*-xylene, and that between 140° and 145° as *o*-xylene ; these limits refer to uncorrected temperatures, i.e., those indicated by a thermometer with its scale only partially immersed in the vapour.

**4. Detection and Estimation of Impurities.**—The impurities of commercial benzoles are principally carbon disulphide, thiophene, paraffin hydrocarbons and naphthalene.

(*a*) CARBON DISULPHIDE. This is *detected* by shaking about 10 c.c. of the benzole or, better, of the first fractions of its distillate, with 5 or 6 drops of phenylhydrazine and leaving the mixture at rest for an hour. In presence of as little as 0·2% of carbon disulphide, a white precipitate of phenylhydrazine phenylsulphocarbazinate is formed.

For the *determination*, the ammonium xanthate (Hoffmann) reaction is used :

A mixture of 50 grams of the benzole with 50 grams of alcoholic potash solution (11 grams of KOH in 90 grams of absolute alcohol) is left for some hours at the ordinary temperature and is then shaken with 100 c.c. of water. The aqueous layer is separated from the benzole, which is washed two or three times with water, the total aqueous liquid being made up to 400 c.c. In this solution, or an aliquot part of it, the potassium xanthate formed is determined volumetrically by means of a standard copper solution (12·468 grams of crystallised copper sulphate per litre).

This is effected by acidifying the aqueous liquid containing the xanthate with acetic acid and then adding the copper sulphate solution until the copper is in excess, i.e., until a drop of the liquid gives the brown coloration with potassium ferrocyanide. The number of c.c. used, multiplied by 0·0076, gives the percentage of $CS_2$ in the aqueous liquid and from this the percentage in the benzole may be calculated.

(*b*) THIOPHENE. This is *detected* by the indophenine reaction. To a few granules of isatin in a porcelain basin, a few c.c. of pure conc. sulphuric acid are added and then the benzole, the liquid being covered with a clock-glass and left to itself for some hours : in presence of thiophene, blue rings form around the isatin granules.

Only benzoles guaranteed free from thiophene are tested for the latter.

(*c*) PARAFFIN HYDROCARBONS (benzines). These are *determined* by transforming the benzoles into the soluble sulpho-acids (Kraemer and Spilker) [1] : 200 grams of the benzole are shaken for 15 minutes in a separating funnel with 500 grams of fuming sulphuric acid (20% $SO_3$), cooled if necessary and left for two hours. The sulphuric acid is removed and the operation repeated twice. The residual unattacked oil floating in the sulphuric acid represents almost the whole of the paraffin hydrocarbons (including naphthenes) contained in the 200 grams of benzole.

[1] Muspratt : *Chemie*, 4th edit., Vol. VIII, p. 34.

For exact determinations, the hydrocarbons remaining suspended in the sulphuric acids employed should be collected. The acid liquors are poured slowly and with shaking on to an equal weight of pounded ice in a flask, the temperature never exceeding 40°. The liquid thus obtained is distilled and the oil separating at the surface of the first 50 c.c. of distillate added to the quantity determined directly. The total oil thus obtained is repeatedly purified with fuming sulphuric acid (20% of anhydride) in lots of 30 grams each until no further diminution in volume takes place. It is then washed with water and measured, the volume, divided by 2, giving the quantity of paraffin hydrocarbons in 100 of the benzole.

(*d*) NAPHTHALENE. 10 c.c. of the benzole are allowed to evaporate spontaneously in a glass dish, any naphthalene present remaining crystallised on the walls of the dish.

**5. Degree of Refining.**—Benzoles may contain larger or smaller quantities of resinous substances not completely removed by refining. The presence of these substances may be detected as follows:

(*a*) WITH SULPHURIC ACID. 5 c.c. are added to 5 c.c. of conc. sulphuric acid in a cylinder with a ground stopper, the mixture being shaken for two or three minutes and the colour of the acid observed. Pure products do not colour the acid at all, and commercial products colour it pale yellow or brown according to the extent to which refining has been carried. The coloration may be measured by comparison with solutions of potassium dichromate in sulphuric acid.

(*b*) WITH BROMINE. 5 c.c. of the benzole are mixed in a beaker with 10 c.c. of dilute sulphuric acid (1 : 5) and a decinormal potassium bromide and bromate solution (9·9167 grams KBr + 2·7833 grams $KBrO_3$ per litre) run in, slowly and with shaking, at intervals of five minutes until the bromine liberated no longer undergoes absorption; this is shown by the orange-yellow coloration of the benzole and by the blue colour imparted to starch-iodide paper. The degree of refining is in inverse ratio to the amount of bromine absorbed (1 c.c. N/10-solution = 0·008 gram Br). The loss during further refining will be 1% per 0·2 c.c. of the bromine solution used.

***

The benzoles most commonly found on the market may come from the distillation of light tar oils or from the distillation of the washing oils obtained by exhaustion of the gas from the manufacture of coke or coal gas by means of heavy oils. These are mixtures in varying proportions of benzene and higher homologues. Examples of the more important characters of these products are as follows (Spilker):

TABLE XL

**Character and Composition of Benzoles**

| Mark and Denomination. | Specific Gravity at 15° C. | Percentage of Distillate at different temperatures. | Composition. | | | |
|---|---|---|---|---|---|---|
| | | | Benzole. | Toluole. | Xyloles. | Higher homologues. |
| I (90% benzole) . . | 0·880–0·883 | 90–93% up to 100° | 84 | 13 | 3 | — |
| II (50% benzole) . . | 0·875–0·877 | 50–53% up to 100°<br>90–93% up to 120° | 43 | 46 | 11 | — |
| III . . . . . | 0·870–0·872 | 90% at 100–120° | 15 | 75 | 10 | — |
| IV . . . . . | 0·872–0·876 | 90% at 120–145° | — | 25 | 70 | 5 |
| V (solvent naphtha) . | 0·874–0·880 | 90% at 130–160° | — | 5 | 70 | 25 |
| VI ,, ,, . | 0·890–0·910 | 90% at 145–175° | — | — | 35 | 65 |
| Heavy benzole . . | 0·920–0·945 | 90% at 160–190° | — | — | 5 | 95 |

These benzoles contain varying proportions of impurities. Thus, thiophene is always present in the earlier of the above marks and carbon disulphide occurs to the extent of 0·2–1% in benzole I and 0–0·5% in benzole II, whilst it is usually absent from succeeding marks. In marks I, II and III, the amount of paraffin hydrocarbons is at most 1%, and in other marks rather more. Pure benzoles are coloured by 0·1 c.c. of the bromide-bromate solution, but the commercial products require 0·6–1%.

As regards the behaviour of the principal commercial products on fractional distillation with a rectifier for the separation of the individual hydrocarbons (*see* above, 3), the following serve as examples:

| | Benzole I. | Benzole II. | Pure commercial Benzole. | Commercial Toluole. | Commercial Xylole. |
|---|---|---|---|---|---|
| First fraction . . . | 1·0% | 0·3% | 0·5% | | |
| Benzole . . . . | 78·8% | 18·3% | 98·0% | 0·3% | 1·3% |
| Intermediate fraction . . | 10·0% | 47·5% | | | |
| Toluole . . . . | 8·0% | 23·7% | 1·5% | 97·3% | |
| Xyloles . . . . | 2·2% | 10·2% | | 2·4% | 96·5% |
| Higher homologues, etc. . | | | | | 2·2% |

The proportions of the three isomerides in commercial xylole are about 76·5 of *m*-, 15 of *p*- and 5 of *o*-xylene.

## NAPHTHALENE

This is marketed in different degrees of purity: *crude*, coloured brown by tar oils and other impurities, and moderately *pure*, in more or less large, white or faintly yellow, lamellar crystals. The tests usually made to determine the purity are as follows:

**1. Melting and Solidification Points.**—These are determined by means of Shukoff's apparatus (*see* Chapter on Mineral Oils, Solid Paraffin, 2), the inner test-tube being half filled with the fused naphthalene and a thermometer reading to 0·1° immersed in it. On immersion the thermometer bulb becomes covered with a layer of solidified naphthalene; it

is then stirred until this layer melts and the temperature noted, this indicating approximately the melting point. The fused mass is then stirred with the same thermometer until naphthalene crystals again begin to form and the column of the thermometer remains stationary for some time. This is the solidifying point, which, with pure naphthalene, corresponds with the melting point.

**2. Presence of Oily Products.**—A packet of 50 grams of the naphthalene wrapped in several thicknesses of filter-paper is subjected in a press to a pressure of about 150 atmos. for 10 minutes, the paper being then examined to see if it is stained by the oil absorbed.

**3. Behaviour towards Petroleum Ether.**—2 grams of the naphthalene are treated in a test-tube with light petroleum to see if a clear, colourless solution is obtained.

**4. Behaviour towards Sulphuric Acid.**—4 grams are heated in a test-tube in a water-bath with 4 grams of conc. sulphuric acid until a clear solution is obtained, the colour being observed. The sulphuric acid solution is poured into about 40 c.c. of water to ascertain if the whole remains clear and colourless.

**5. Stability towards Light.**—2 grams of the naphthalene on a clock-glass are left for 1–2 hours in a desiccator over conc. nitric acid (not fuming), the naphthalene being then examined to see if it has remained unaltered or if it is coloured.

***

*Pure* commercial naphthalene is white or slightly yellow and melts at 79·6–79·8°; it should not mark paper (test 2) and should volatilise completely if heated on a water-bath; test 3 should yield a clear solution, at most pink or reddish, which should remain clear on dilution; it should dissolve completely in petroleum ether (test 4) and should remain unchanged when subjected to test 5 (slightly impure naphthalene becomes pale pink).

## ANTHRACENE

Commercial anthracene is always impure, containing principally naphthalene, methylanthracene, carbazole, paraffin wax, phenanthrene, etc. . The technical examination of crude anthracene is limited to the determination of the anthracene content and to tests for the presence of impurities which are harmful in the coal-tar colour industry.

**1. Determination of the Anthracene.**—Luck's method, based on the oxidation of anthracene to anthraquinone by means of chromic acid, is usually employed. In a flask with a capacity of about half a litre, fitted with a tapped funnel and a reflux condenser, a boiling solution of 1 gram of the anthracene in 45 c.c. of glacial acetic acid is treated with a solution of 15 grams of crystallised chromic acid in 10 c.c. of glacial acetic acid and 10 c.c. of water, this liquid being added in small quantities so that the whole addition requires about 2 hours. The solution is boiled for two hours longer, then left to itself for 12 hours, next mixed with 400 c.c. of cold water and left at rest for 3 hours. The precipitated anthraquinone is collected on a filter and washed first with cold water, then with faintly alkaline

boiling water (1 gram KOH per litre) until the filtrate no longer becomes turbid on acidification and finally with boiling water until the alkalinity is removed. The contents of the filter are washed by means of a fine water jet into a small porcelain dish, the water being evaporated and the residue dried at 100° and heated for 10 minntes on a boiling water-bath with 10 c.c. of fuming sulphuric acid (D 1·88). The dish is subsequently left in a moist place for 12 hours, the contents diluted with 200 c.c. of cold water, and when cold the anthraquinone filtered, washed as before, placed in a tared dish, evaporated, dried at 100° and weighed. For greater exactness the anthraquinone is evaporated and the residual ash determined: anthraquinone × 0·8558 = anthracene.

**2. Detection of Impurities.**—Among the more common impurities which are harmful in certain applications of crude anthracene, e.g., in the preparation of alizarin, are methylanthracene, carbazole, paraffin wax and phenanthrene. These substances are detected as described in the following paragraphs; for their quantitative determination, which is carried out only rarely and for special purposes, special works must be consulted.[1]

(*a*) METHYLANTHRACENE. When anthracene containing methylanthracene is oxidised by chromic acid, as described above, methylanthraquinone is produced, this forming threads variously twisted rather than needles like anthraquinone. Methylanthraquinone is distinguished from the latter also by its great solubility in benzene.

(*b*) CARBAZOLE. The anthracene is extracted with ethyl acetate, the solution evaporated, and the residue treated with a few drops of ethyl acetate to which are added some drops of nitrobenzene and a little phenanthrenequinone. The presence of carbazole is shown by the formation of characteristic, lamellar, copper-coloured crystals.

(*c*) PARAFFIN WAX. 10 grams of anthracene are treated with 100 c.c. of ether, the ethereal solution separated and evaporated and the residue treated with 200 grams of fuming sulphuric acid (20% of anhydride) for three hours at 100°. The whole is poured into 500 c.c. of water and, after cooling, the paraffin wax separated at the surface is filtered off, washed well with water, the filter allowed to dry and then moistened with alcohol, and the paraffin collected by adding ether. The ethereal solution thus obtained is evaporated, and the residue, dried at 105°, gives the solid paraffin in the sample.

(*d*) PHENANTHRENE. A certain quantity (1 kilo) of the product to be tested is dissolved in the hot with double its volume of toluene. After cooling, the crystallised anthracene and carbazole are separated and the mother-liquor distilled, the portion passing over between 300° and 340°—which contains the greater part of the phenanthrene—being collected apart. 20 grams of this fraction are boiled for half an hour in a reflux apparatus with 30 grams of picric acid and 300 c.c. of xylene and the liquid allowed to cool for 24 hours; the phenanthrene picrate which separates is crystallised from alcohol in reddish-yellow needles melting at 145°.

[1] Lunge: *Coal-Tar and Ammonia* (London, 1916), p. 640.

Commercial *crude anthracene* forms masses of yellowish to brown crystalline scales with an odour resembling that of naphthalene; according to the degree of purification, it contains 30–39% of anthracene (English anthracene A contains 40–50%).

*Pure anthracene* forms white, tabular crystals with a blue fluorescence, m.pt. 216·5°, b.pt. 360°; it is slightly soluble in alcohol, ether, benzine, carbon disulphide and cold benzene, and readily soluble in the hot in benzene, pyridine and glacial acetic acid.

## CARBOLIC ACID

*Crude* and *pure* carbolic acid are on the market. The former is of somewhat variable composition, the name being often given to yellowish or dark brown carbolic oils containing, besides varying quantities of neutral tar oils, also phenol and its homologues (mainly cresols), whereas it is also used to designate pale red products rich in phenols and crystallising more or less easily when cooled. The pure product is colourless or pale red, crystallisable and soluble in 15 parts of water.

In very impure products the determination of the phenols and neutral oils is carried out as in 2; in the others, the water, solidification point, and the solubility are determined (3, 4 and 5) and, if required, the quantitative estimation according to Koppeschaar (*see* 2).

**1. Characteristic Reactions of the Phenols.**—The following reactions are used:

(*a*) The aqueous solution of a phenol gives a violet coloration with dilute ferric chloride solution (provided mineral and organic acids, alcohol, ether and glycerine are absent).

(*b*) When heated gently with a little ammonia and a few drops of sodium hypochlorite, the aqueous solution of a phenol gives an intensely blue coloration.

(*c*) The substance is shaken with water and the aqueous solution treated with bromine water: if it is a phenol, a voluminous, white precipitate of tribromophenol, at first flocculent and afterwards crystalline, is produced. It is soluble in alkali and is reprecipitated on acidification of the alkaline solution. The tribromophenol reaction (*Landolt's reaction*) is sensitive to about 1 part in 44,000. The cresols and also other organic compounds are precipitated by bromine water.

(*d*) A very sensitive reaction is as follows: About 1 c.c. of the oil to be examined is shaken with 1 c.c. of alcohol, after which 2 c.c. of water and 1 c.c. of about 1% nitrazole solution (fresh) are added and again shaken: addition of a little caustic potash then colours the aqueous layer an intense red in presence of phenols.

**2. Determination of Phenols and Neutral Oils.**—The approximate determination of the phenols and neutral oils in crude phenol may be rapidly carried out by shaking a measured volume of the sample with double its volume of 10% sodium hydroxide solution in a stoppered graduated cylinder, allowing to stand and reading the volume of the neutral oils which separate; subtraction of this volume from that of the substance used gives the quantity of phenols. To facilitate the separation of the neutral oils it is sometimes

convenient to dilute the sample with an equal volume of ligroin, the volume of the latter being then subtracted from that of the neutral oils separating.

As a control, the alkaline layer may be separated, acidified in a graduated cylinder and the volume of the phenols separating read.

More exact results are obtained as follows: 120 grams of the carbolic acid to be examined are distilled until only about 8 grams of residue remain in the flask, the distillate being dissolved in ether and shaken repeatedly in a separating funnel with 10% caustic soda solution. The total alkaline liquid is washed several times with ether and then acidified with hydrochloric acid diluted with an equal volume of water, the acid liquid thus obtained being extracted repeatedly with ether in a separating funnel to dissolve the phenols. The ethereal solution of the latter is washed with water and placed in a weighed flask, almost all the ether being distilled off; the flask is then closed by a stopper through which passes a vertical bulb tube and a thermometer, and the last portions of ether then evaporated, care being taken that the temperature does not exceed 100°; the cold flask is then re-weighed, the increase in weight representing the phenols.

When the phenol is *not accompanied* by its homologues (cresols, etc.), it may be determined volumetrically by Seubert and Beckurts' modification of Koppeschaar's method:

Use is made of a solution of potassium bromide and bromate in the proportions, $5KBr + KBrO_3$, which in presence of an acid liberates bromine according to the equation: $5KBr + KBrO_3 + 6HCl = 6KCl + 3Br_2 + 3H_2O$. About 1 gram of the sample (or more, if poor in phenol) is weighed and dissolved in water to a litre, 25 c.c. of this solution being vigorously shaken, in a bottle with a ground stopper, with 50 c.c. of potassium bromide solution (6 grams[1] per litre), 50 c.c. of potassium bromate solution (1·671 gram per litre), and 5 c.c. of conc. sulphuric acid. After a rest of 15 minutes, 10 c.c. of potassium iodide solution (125 grams per litre) are added and the iodine liberated titrated with decinormal thiosulphate in presence of starch paste. The amount of phenol contained in the 25 c.c. of solution used is found by multiplying the number of c.c. of decinormal thiosulphate used by 0·001567 and subtracting the product from 0·047.

**3. Determination of the Water.**—(*a*) In *crude products*, this is effected by distilling 100 c.c. through a condenser and collecting the water in a graduated cylinder until about 10 c.c. of phenols are collected under the water. The volume of the upper layer, plus 5 c.c., gives the percentage of water in the product distilled. If any neutral oils are floating on the water, their volume is subtracted.

(*b*) With *less impure products*, 50 c.c. of the substance are shaken, in a 100 c.c. graduated cylinder reading to 0·2 c.c., with 25 c.c. of saturated salt solution and the aqueous layer allowed to separate: its increase in volume indicates the amount of water in the sample.

**4. Determination of the Solidification Point.**—This is made in the Shukoff apparatus (*see* Mineral Oils, Paraffin, 2), 50 grams of the fused phenol being introduced into the inner tube and allowed to cool slowly

[1] Owing to the slight admixture of potassium chloride, 6 grams are taken instead of 5·95.

while stirred with the thermometer. When the temperature has fallen below the solidifying point of pure phenol (42°), a crystal of phenol is added, the mass beginning to crystallise and the temperature rising and then remaining stationary. The highest temperature shown represents the solidifying point of the product tested.

5. **Solubility.**—1 c.c. of the material, shaken in a graduated cylinder with 15 c.c. of water, should give a perfectly clear solution if the product is pure. The more impurities present, the more insoluble matter remains.

***

Pure carbolic acid has the melting (solidifying) point, 40–42°, and the boiling point, 183–184°. Products are sold, however, with lower melting points (down to 32°), this resulting from the presence of small quantities of moisture and cresols.

## PYRIDINE

This is obtained mainly from the distillation products of tar and is sold crude or pure. *Crude pyridine* (*pyridine bases*) consists essentially of bases of the pyridine and quinoline groups, etc., and may contain other aromatic bases, pyrrole and ammonia. It is a colourless or yellowish liquid of a penetrating and peculiarly unpleasant odour, readily volatile and inflammable, soluble in water. *Pure pyridine* is colourless and miscible in all proportions with water or ether, b.pt. 116–117°, D 0·980. In the crude state it is used mainly for the denaturation of spirits for industrial purposes. The following are the tests made:

1. **Colour.**—The colour is compared with that of a solution containing 2 c.c. of decinormal iodine solution to a litre, using two glass tubes 150 mm. long and 15 mm. in diameter, closed with glass discs (polarimeter tubes may be used).

A colorimeter is more practicable (*see* Mineral Oils).

2. **Behaviour towards Cadmium Chloride.**—10 c.c. of a solution of 1 c.c. of the pyridine in 100 c.c. of water are shaken vigorously with 5 c.c. of a solution of fused cadmium chloride (5 grams in 100 of distilled water). A copious, crystalline precipitate should form, this being then filtered through a 9 cm. filter-paper (weighing 0·45–0·55 gram), dried for an hour at 50–70° and weighed.

3. **Detection of Ammonia.**—Ammonia in pyridine is readily detected by means of phenolphthalein or litmus paper, on which the pyridine has no action.

Small quantities of ammonia are best tested for by means of Nessler's reagent (*see* Potable Waters), 5 c.c. of the latter being added to 10 c.c. of a 1% solution of the pyridine: if no ammonia is present, only a white precipitate is formed.

4. **Distillation.**—100 c.c. are distilled from a flask of glass or, in industrial practice, of copper of about 200 c.c. capacity and with a short neck into which is inserted a bulb rectifier of the dimensions shown *in Fig. 39*, this being joined to a condenser at least 40 cm. long and fitted

with a thermometer with its bulb central. The flask is heated over the aperture in an asbestos card in such a manner that 5 c.c. distil per minute; when the temperature reaches 140°, the heating is interrupted, the liquid that comes over being still collected and the volume of the distillate measured. The distillation is then continued up to 160° and the volume of the distillate measured.

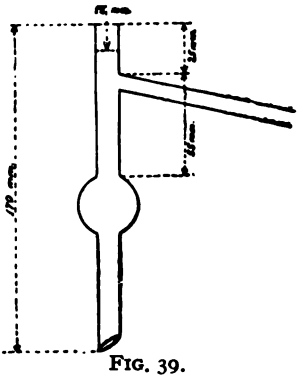

FIG. 39.

**5. Behaviour towards Water.**—50 c.c. of the pyridine are treated with 100 c.c. of water to ascertain if the two liquids mix completely and if the solution is clear or more or less opalescent. The opacity may be determined best by looking through the mixture in a tube such as is indicated under 1 (above) and determining the possibility or otherwise of reading print of definite dimensions.

**6. Behaviour towards Caustic Soda.**—In a graduated cylinder with a ground stopper, 20 c.c. of the pyridine are shaken with 20 c.c. of caustic soda solution, D 1·4 (50 grams of sodium hydroxide in 100 c.c.) and left for an hour; the volume of the upper layer, consisting of the pyridine bases, is then read. The difference between this volume and 20 c.c. gives the water content.

**7. Determination of the Bases.**—10 c.c. of the pyridine are diluted with water to 100 c.c. and 10 c.c. of this solution titrated with normal sulphuric acid until a drop of the liquid produces on Congo red paper [1] a blue ring, which quickly disappears. The result is expressed by indicating the number of c.c. of normal acid employed.

A more exact determination is obtained by François' gravimetric method,[2] based on the insolubility in anhydrous ether of the additive compound of pyridine hydrochloride with gold chloride. About 0·1 gram of the material is weighed into a porcelain basin and treated with water, 20–30 drops of hydrochloric acid and excess of gold chloride solution, a precipitate being formed and the liquid remaining deep yellow. The whole is evaporated to dryness on a water-bath and, when all the hydrochloric acid is eliminated, washed by decantation with anhydrous ether as long as any colour is still removed (to eliminate the excess of gold chloride). The precipitate remaining in the dish is calcined and the metallic gold weighed: Au × 0·401 = pyridine, when pure pyridine is taken. With crude pyridine, the weight of the gold must be multiplied by the coefficient 0·5583 (deduced from the mean molecular weight of the bases, 110).

***

The requirements for pyridine bases to be used for denaturation are:

Test 1: should remain colourless or less coloured than the solution of iodine indicated.

[1] Prepared by immersing chemically pure filter-paper in 1% aqueous Congo red solution and allowing to dry.

[2] *Comptes rendus*, 1903, Vol. 137, p. 329.

Test 2 : the weight of the precipitate obtained with cadmium chloride should not be less than 0·025 gram.

Test 3 : ammonia absent.

Test 4 : at least 50 c.c. should distil below 140° and not less than 90 c.c. below 160° (including the preceding amount).

Test 5 : should mix completely with water and give a clear or barely opalescent solution.

Test 6 : the layer of pyridine bases separating should occupy at least 18·5 c.c.

Test 7 : not less than 9·5 c.c. N-sulphuric acid should be used.

## CHAPTER VIII

# MINERAL OILS

## AND PRODUCTS DERIVED FROM THEM

*Crude petroleum* yields various industrial products which may be grouped in the following classes:

1. *Light oils* (gasoline and naphtha), b.pt. below 150° C.

2. *Lamp oil* or *kerosene*, principally the fractions boiling between 150° and 310°.

3. *Medium oils* (gas oils), intermediate to lamp oil and the heavy oils.

4. *Heavy oils*, which include the fractions distilling above 300–310° and treated to render them suitable as lubricants.

5. *Residuum*, which consists of the residue left after distillation of the light and medium oils and sometimes also of part of the heavy oils, without further treatment.

6. *Vaseline*, composed of hydrocarbons semi-solid at the ordinary temperature.

7. *Solid paraffin* or *paraffin wax*, formed of solid hydrocarbons.

Products analogous to these are obtained by distillation of *bituminous shales* and are termed *shale oils*; these also yield *light oils* (shale spirit), *burning oils*, *heavy oils*, and a considerable quantity of solid paraffin.

Similar to the last is *ceresine*, obtained by refining *ozokerite* or *earth wax*. A product of similar appearance to ozokerite is *montan wax*.

These products are treated in the following articles, together with *lubricants*, now largely used industrially and mostly having a basis of mineral oil.

In sampling these products, reference may be made to the directions given for tar.

## CRUDE PETROLEUM

This is usually a brown or blackish liquid, but sometimes reddish or yellow, with a characteristic bituminous odour; it is often turbid owing to the presence of suspended water and solid substances.

The tests to be made are partly physical and partly chemical.

### 1. Physical Examination

**1. Determination of the Specific Gravity.**—The hydrometer or the Westphal balance is used, or, if the amount of substance available is small

or if very exact results are required, the picnometer. The determination should be made at 15° or referred to 15°, the mean temperature coefficient of specific gravity being 0·0007 (0·0006–0·0008) per 1°.

**2. Fractional Distillation.**—In order that concordant results may be obtained, this should always be carried out under certain definite conditions and in an apparatus of fixed dimensions. Engler's flask, shown in Fig. 40, is generally used. 100 c.c. of the oil are placed in the flask, which is connected with a condenser 60 cm. long and heated, both the flame and the flask being protected with a sheet metal mantle.

The initial temperature of distillation is that at which the first drop of distillate issues from the condenser fitted to the side-tube of the flask. The velocity of distillation should be such that two drops pass over per second. The distillate is collected in several graduated cylinders, or in a single 100 c.c. cylinder in which the volumes of the distillates at the different

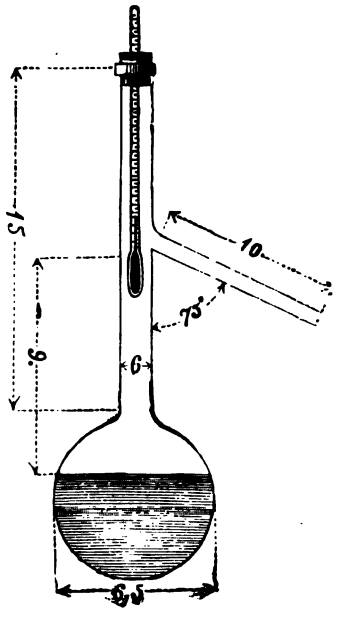


FIG. 40

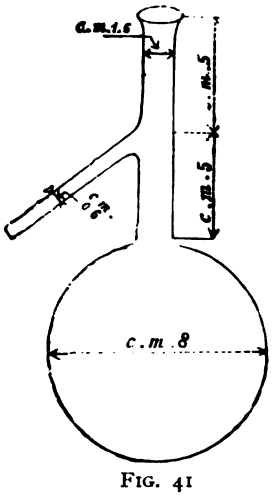


FIG. 41

temperatures are read off successively. The distillation is at an end when the flask contains only residuum or white fumes appear. The fractions usually collected are:

Benzine: up to 150°

Lamp oil: 150–300°.

Heavy oils: above 300°.

In the Italian Customs Laboratory, for the determination of the fractions distilling below 310° for fiscal purposes, use is made of a flask similar to the preceding but of the dimensions shown in Fig. 41. 100 c.c. of the petroleum are then distilled, the flask being heated over a gauze by a small flame; subsequently the flame is enlarged, and it may finally be necessary to surround the flask with an asbestos mantle. The rate of dis-

tillation should be such that about 2 grams of distillate collect per minute. The weight of the distillate up to 310° is determined.

If the mineral oil contains much water, it is convenient to dehydrate it by means of calcium chloride and to decant it before distillation in order to avoid bumping during the heating.

**3. Flash Point.**—The *flash point* of an oil is the temperature corresponding with the initial evolution of vapour forming with air a mixture capable of exploding in contact with a flame, or, more accurately, the temperature at which such vapour can be detected under definite experimental conditions.

This determination is made with crude petroleum as with light oils (*see* later). With crude petroleums poor in light oils, however, the high flash point requires the use of the apparatus employed with lamp oil or heavy oils (*see* the paragraphs concerned).

**4. Temperature of Ignition.**—This is the temperature at which the mineral oil, coming into contact with a flame, ignites and continues to burn. For its determination, *see* Light Mineral Oils.

**5. Calorific Power.**—As a rule this is determined only when the crude petroleum is to be used as a fuel, as is the case with that from certain localities (Texas, California); the Mahler bomb calorimeter is used (*see* Fuels). If the petroleum is poor in light oils, 1–1·5 gram of it is weighed directly into the capsule for holding the fuel, but if rich in volatile matter it is well to weigh it in a small glass bulb with the ends drawn out, the igniting wire being passed through the bulb; the bulb is placed in the capsule and just before the bomb is closed the two ends are broken in order to facilitate access of the oxygen to the liquid.

## 2. Chemical Tests

**1. Determination of the Water** (Marcusson's method).[1]—100 c.c. of the product are mixed with 50 c.c. of xylene and the mixture distilled, in presence of a few scraps of pumice, best in an oil-bath until the water passes over. The distillate is collected in a graduated cylinder and the volume of the lower aqueous layer measured.

**2. Determination of the Suspended Solid Matter.**—The oil is shaken with at least 20 times its volume of benzene (to dissolve any suspended pitch and asphalt), filtered after standing for some hours, and the residue on the filter washed with benzene, dried and weighed.

**3. Determination of the Sulphur.**—This may be carried out by Eschka's method (*see* Fuel) or in the Mahler calorimetric bomb. With Eschka's method, 1 gram of the mineral oil is mixed with sufficient of the mixture of magnesia and sodium potassium carbonate to give a dry powder, which is covered in the crucible with a layer of the mixture.

In the bomb, the determination is made simultaneously with that of the calorific power, the sulphur undergoing conversion to sulphuric acid.

When the combustion is complete, the gas formed is passed through about 25 c.c. of 8% potassium carbonate solution, the apparatus being then rinsed

[1] J. Marcusson: *Laboratoriumsbuch für die Industrie der Oele und Fette* (1911).

out with about 300 c.c. of water in all. The whole is then evaporated on a water-bath to about 50 c.c., and filtered, the filter being washed with hot water; the filtrate is acidified with hydrochloric acid and the sulphuric acid precipitated as barium sulphate: $BaSO_4 \times 0{\cdot}1374 = S$.

This method is also applicable to all derivatives of crude petroleum and always gives good results.

**4. Determination of the Solid Paraffin.**—This is effected by Holde's method, after fractions below 300° have been eliminated. To this end, 100 grams of the crude petroleum are rapidly distilled, the distillate up to 300° being collected. If the residue from the distillation is dark and turbid, as is usually the case, it also should be distilled—the thermometer and condenser having been removed—until only fixed, carbonaceous residue remains in the retort. The distillate above 300° (or the oil remaining in the flask if it is not distilled) is weighed and treated as follows in the apparatus shown in Fig. 42.

This consists of a vessel surrounded by felt and containing an ice-salt mixture in which are immersed the tubes containing the test material and the funnel used for the filtration; the funnel is connected with a pump flask. The apparatus is provided with another tube (5) by means of which the water from the freezing mixture may be run off.

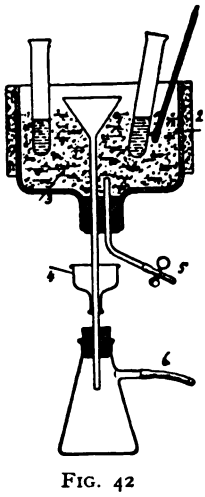

FIG. 42

Of the oil distilled as described above, 5–10 grams are placed in a wide test-tube and dissolved in the necessary quantity of a mixture in equal proportions of absolute alcohol and ether. The tube is placed in the freezing mixture so as to keep it at about −20°, and, while the liquid is stirred with the thermometer, the alcohol-ether mixture added until the oily drops which separate are redissolved and only the solid paraffin remains out of solution. The liquid is then filtered by means of a pump on the funnel kept between −15° and −20°, the residue being washed with cooled alcohol-ether mixture (if the solid paraffin is soft, it is well to wash with a mixture of 2 parts of alcohol and one of ether) until a few c.c. of the washing liquid leave no appreciable oily residue on evaporation. The remaining solid paraffin is then dissolved on the filter in hot benzene into a tared glass dish, the benzene being evaporated on a water-bath—which finally should boil vigorously—and the dish dried for 15 minutes at 105°, cooled in a desiccator and weighed. The percentage of solid paraffin in the original oil is then calculated.

By this method, a small quantity of solid paraffin remains dissolved in the alcohol-ether mixture; the result obtained should, therefore, be increased by 0·2% for a very fluid oil, or by 0·4% for an oil so rich in solid paraffin that it deposits it at 15°.

**5. Detection and Determination of the Asphalt.**—Usually two varieties of asphalt are distinguished in crude petroleums, namely, *hard* and *soft asphalt.*

1. DETECTION. (a) *Hard asphalt.* About 0·3 gram of the oil is shaken in a test-tube with 20 c.c. of petroleum ether (D not above 0·7) and left overnight; any hard asphalt present is deposited in blackish flocks soluble in benzene.

(b) *Soft asphalt.* About 0·5 gram of the oil is dissolved in a test-tube in 15 c.c. of ether and the liquid treated with 7·5 c.c. of 96% alcohol; any soft asphalt present is precipitated in the form of flocks, which unite to a viscous mass adherent to the walls of the tube and soluble in benzene.

2. QUANTITATIVE DETERMINATION. (a) *Hard asphalt.* About 5 grams (or more, with a product poor in asphalt) of the oil are shaken in a litre flask with 200 c.c. of the petroleum ether used for the qualitative test and left at rest for a day. The liquid is then decanted on to a pleated filter, to which also the insoluble substances are transferred, flask and filter being washed with benzine until a few drops of the filtrate leave no oily residue on evaporation. The insoluble residue on the filter is at once dissolved in hot benzene, the solvent evaporated in a tared dish and the residue dried at 105° and, when cold, weighed.

(b) *Soft asphalt.* 5 grams of the product are dissolved, in a bottle fitted with a ground stopper and of about 300 c.c. capacity, in 25 volumes of ether, 12·5 volumes of 96% alcohol being run in to the solution, drop by drop and with shaking, from a burette. After standing for 5 hours at 15°, the liquid is filtered and the bottle and filter washed with the alcohol-ether mixture (1 : 2) until the washing liquid leaves no oily residue, or at most traces of pitchy substances, on evaporation.

The precipitate, which may contain solid paraffin as well as asphalt, is dissolved in benzene, the solution evaporated, the residue treated repeatedly in the hot with 96% alcohol (about 30 c.c.) until the alcoholic extracts no longer deposit solid paraffin on cooling. The residue, consisting only of the soft asphalt, is dried for 15 minutes at 105° and weighed.

For precipitating the asphalt in mineral oils, besides benzine and alcohol-ether, also butanone,[1] amyl alcohol and ethyl acetate have been proposed.

Different solvents precipitate asphaltic substances in different quantities and of different qualities, so that the analytical results are only relative and not absolute.

**6. Behaviour towards Concentrated Sulphuric Acid.**—Concentrated sulphuric acid precipitates from crude petroleum asphaltic and pitchy substances in larger or smaller quantity. In many cases it is, therefore, useful to determine these substances, this being done in the following manner.

In a graduated cylinder with a ground stopper 20 c.c. of the oil are dissolved in 80 c.c. of petroleum ether (D 0·700, and ascertained by preliminary trial to be unattacked by conc. sulphuric acid), the solution obtained being shaken for a minute with 10 c.c. of conc. sulphuric acid (66° Baumé) and left until the liquid separates sharply into two layers. From the volume of the dense, black, lower layer is subtracted the volume of acid added (10 c.c.), the difference representing the quantity of asphalt and pitchy substances in 20 c.c. of the oil.

[1] Schwarz: *Chem. Zeit.*, 1911, 35, p. 1417.

*Crude petroleums* have *specific gravities* varying from 0·771 to about 1·020, the Russian being usually denser than the American.

As regards *fractional distillation*, good American crude petroleums generally contain much light oil and lamp oil, while their heavy fractions contain marked quantities of solid paraffin. Russian petroleums, however, furnish less quantities of light and middle distillates, whilst the heavy fractions abound, although these are poor in paraffin wax. Galician and Rumanian petroleums are mostly rich in middle fractions, and their heavy ones contain solid paraffin. Italian petroleums are usually richer in light and middle than in heavy fractions.

The *flash point* is mostly near 0°, but varies with the content of light oils.

The *sulphur* content is generally low (less than 1%), but in some cases, e.g., in Texan and Californian petroleums, more is found (4–5%).

The *calorific power* of crude petroleums is as a rule 10,000–11,000 cals. and diminishes as the specific gravity increases. Petroleums poor in the lighter fractions are more particularly used directly as fuels, e.g., those of Texas, California and Mexico; petroleums with little sulphur are preferable for this purpose, but those with larger proportions may also be used.

## LIGHT MINERAL OILS

### (Benzine)

These are volatile, mobile, colourless, or pale yellow liquids, usually clear but sometimes opalescent, in which case the presence of water is to be suspected.

The following tests and determinations are made:

**1. Determination of the Specific Gravity.**—This is made at 15° by the methods indicated for crude petroleum.

For fiscal purposes the Italian Customs authorities use two thermo-aerometers, one for the densities 0·610–0·700 and the other for 0·680–0·770. By means of tables published on the authority of the Ministry of Financc,[1] density readings made at other temperatures are reduced to 15°. If the weight of any consignment is known, the volume can then be calculated.

Besides as a means of characterising the various products comprised under the name light petroleum oils, the specific gravity may serve as an indication of the presence of benzoles, oil of turpentine or light resin oils, all of these having much higher specific gravities—0·86 or more.

**2. Distillation.**—Use is made of the flask already described for crude petroleum, this being connected with a good condenser and heated on a sand-bath with a lamp the flame of which is completely enclosed in a wire gauze cage, so that ignition of the vapours in case the flask breaks may be avoided.

The temperature at which the distillation commences is noted and the distillate collected either in a graduated cylinder, the volume for each 10° being observed, or in a separate tared vessel for each fraction, the vessel being afterwards reweighed. If the whole of the liquid does not distil over below 150°, the distillation is stopped at this temperature and the residue in the flask weighed.

[1] Tables for the determination of the density and volume at 15° of mineral oils, Rome, 1912.

When a more thorough separation of the different fractions is desired, a flask surmounted by a dephlegmator may be used.

With very light, rectified oils, it is useful to evaporate a portion on the water-bath to ascertain if any residue remains, or to allow a little to evaporate spontaneously on a filter-paper to see if any oily spot is left.

Where exact results are required, allowance must be made for the atmospheric pressure when this varies by as much as $\pm$ 5 mm. from the normal (760 mm.).

**3. Flash Point.**—For this purpose use is made of the inner vessel *A* of the Abel apparatus (*see* Lamp Oil, Physical Tests, 4), this being placed in a metal vessel about 6 cm. high and 9 cm. in diameter containing alcohol; this vessel, in its turn, is placed in a larger metal vessel, also containing alcohol and surrounded with felt. Solid carbon dioxide is introduced into the alcohol until the temperature in the liquid to be examined reaches $-50°$ or $-60°$; the temperature is then allowed to rise slowly and the observations begun as with lamp oil.

This determination is seldom made, as it is known that naphtha has a low flash point, which is generally far below 0°, although with some of the heavier types it may be slightly above 0°.

**4. Temperature of Ignition.**—After the flash point has been determined, the cover of the vessel *A* is removed and for every 0·5° rise of temperature a flame is brought near to the surface of the liquid. The temperature of ignition is taken as that at which persistent combustion of the liquid itself takes place.

This determination also is rarely made for the reasons indicated above, the temperature of ignition being only a few degrees (3 or 4) above the flash point.

**5. Degree of Refining.**—The extent of rectification of a light oil is indicated by the following tests:

(*a*) The oil is shaken with an equal volume of conc. sulphuric acid to ascertain if the latter appears coloured after separation.

(*b*) The oil is shaken with boiling water and the latter subsequently tested with litmus and with barium chloride.

(*c*) The liquid is boiled for a few minutes with alcohol containing a few drops of ammonia and then treated with silver nitrate to see if any brown coloration develops.

**6. Detection and Determination of Benzoles.**

(1) DETECTION. (*a*) According to Holde, tar-pitch, previously washed with petroleum benzine (D 0·70–0·71) until the latter dissolves no more, is shaken with the light oil under examination. The latter becomes yellow or brown if tar benzoles are present.

Not less than 5–10% of benzoles are detectable in this way.

(*b*) 5 c.c. of the oil, in a flask fitted with a reflux condenser and immersed in a beaker of water, are treated with small quantities of fuming nitric acid until evolution of red vapours ceases (20 c.c. of acid usually suffice). At the end of the reaction, the contents of the flask are poured into a graduated 100 c.c. cylinder containing 60% alcohol. The flask is

washed out with alcohol of the same concentration, this being poured into the cylinder and the volume made up to 100 c.c. and the whole shaken. Any nitro-derivatives formed from benzoles present pass into solution in the alcohol, while the mineral oil remains undissolved; if the volume of the latter has been diminished by 5 c.c., it is concluded that the oil contained benzoles.

This procedure is valid only for light oils composed of paraffin hydrocarbons, which are not attacked by nitric acid.

2. QUANTITATIVE DETERMINATION. This is effected by Krämer and Böttcher's method, which is based on the absorption of aromatic hydrocarbons by sulphuric acid of D 1·84 at 15°, this being prepared from 80 parts of conc. acid and 20 parts of fuming acid. In a flask holding about 75 c.c., surmounted by a long neck graduated in 0·1 c.c. for 50 c.c., 25 c.c. of the oil are shaken for 15 minutes with 25 c.c. of the above sulphuric acid. After a rest of 30 minutes, concentrated sulphuric acid is poured into the flask until the layer of benzine is entirely in the graduated neck, the volume of this being read off after the lapse of an hour. The difference between this volume and the original one represents the aromatic hydrocarbons.

**7. Oil of Turpentine.**—The procedure followed is that indicated for the detection of mineral oils in oil of turpentine (*see* Chapter on Turpentine and its Products: Oil of Turpentine, 9, in Vol. II).

***

*Crude light oils* are usually yellowish and often contain a certain quantity of less volatile oils, but the *rectified* products should be colourless and should give negative results with the tests described under 5 (above).

*Rectified light oils* are subdivided, according to the temperature at which they distil, into different products, named differently in various countries. Usually the following products are distinguished:

| Name. | Specific Gravity. | Temperature of Distillation. |
|---|---|---|
| Light petroleum ether (Gasoline I) | 0·620–0·660 | 30–80° |
| Heavy petroleum ether (Gasoline II, Light benzine) | 0·660–0·680 | 30–95° |
| Benzine for pleasure automobiles (Petrols) | 0·680–0·705 | 60–100° |
| Benzine for ordinary automobiles (Petrols) | 0·690–0·725 | 60–120° |
| Benzine for heavy automobiles (Petrols) | 0·720–0·770 | 60–150° |
| Benzine properly so-called (Naphtha C) | 0·670–0·720 | 60–100° |
| Ligroin (Naphtha B) | 0·707–0·730 | 80–120° |
| Cleaning oil, Naphtha (Naphtha A) | 0·720–0·750 | 120–150° |
| Substitute for oil of turpentine | 0·730–0·750 | 110–150° |

The limits indicated for the boiling points of petrols are not always alone to be taken as a basis for judging of their quality, as this depends essentially on the respective proportions of the *various fractions* distilling between such limits. For instance, some brands of benzine distil mainly below 90°—these being the best—while with others, more than one-half distils above 90°, these being the least valuable.

The calorific power of petrol is about 11,000–12,000 cals.

## LIGHTING OIL

Paraffin oil or kerosene, used for lighting purposes, is a clear mobile liquid, sometimes colourless, but usually more or less yellow and fluorescent and of characteristic odour. Physical as well as chemical tests are made.

### 1. Physical Tests

**1. Colour.**—The colour of lamp oil may be used as a basis for commercial contracts. Its intensity is determined by Stammer's colorimeter (Fig. 43), which consists of two vertical brass cylinders blackened inside, one of them, closed at the bottom by a glass, being charged with the liquid to be examined; in the other cylinder is inserted a standard glass coloured with uranium oxide to a definite intensity, and under both cylinders is a white reflecting surface. By means of two prisms, the two colours to be compared are observed in the two halves of the circular field of the eyepiece. The depth of the liquid may be varied by vertical displacement of the system of prisms along with a cylinder closed at the bottom by a glass disc and dipping into the cylinder of liquid. When uniformity of the field has been attained the depth of the liquid giving a colour intensity equal to that of the standard glass is read off on a scale.

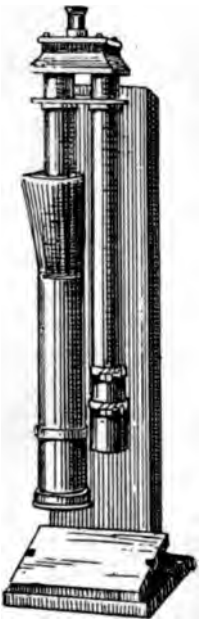

FIG. 43

The four grades of colour usually distinguished in the trade, with the corresponding depths in Stammer's colorimeter are:

| | | |
|---|---|---|
| Standard white. . . . | 50 mm. | |
| Prime white . . . . | 86·5 ,, | |
| Superfine white . . . | 199 ,, | |
| Water white . . . . | 310 ,, | or more |

In England and Russia, use is largely made of the Wilson colorimeter,[1] which contains four standard coloured glasses corresponding with the different commercial grades.

**2. Determination of the Specific Gravity.**—As with crude petroleums, at 15°.

For determining the density of lamp oil for fiscal purposes, the Italian Customs authorities use a thermo-aerometer graduated from 0·750-0·840, and tables of temperature corrections have been prepared.[2]

**3. Fractional Distillation.**—As with crude petroleum.

**4. Flash Point.**—Many forms of apparatus have been devised for this purpose. The results obtained are purely conventional and vary from

[1] Boverton Redwood: *Petroleum*, London, 1913.

[2] Tables for the determination of the density and volume at 15° of mineral oils, Rome, 1912.

one form of apparatus to another, so that comparable data are obtainable only with one and the same instrument under identical conditions.

The apparatus used officially in Italy and also in Great Britain, Germany and Austria is that of Abel, improved by Pensky (Fig. 44). The oil is placed in a brass cylinder *A*, tinned inside and furnished with a gauge index *l*. Its cover carries a thermometer *t* with a scale extending from 10° to 50° and divided into half-degrees, and a clockwork mechanism *m* set in motion by a lever *a*. Pressure of the latter opens automatically a small window in the cover and at the same time lowers a small flame in *b* to the aperture and then raises it again, the window immediately closing. The entire movement should occupy two seconds.

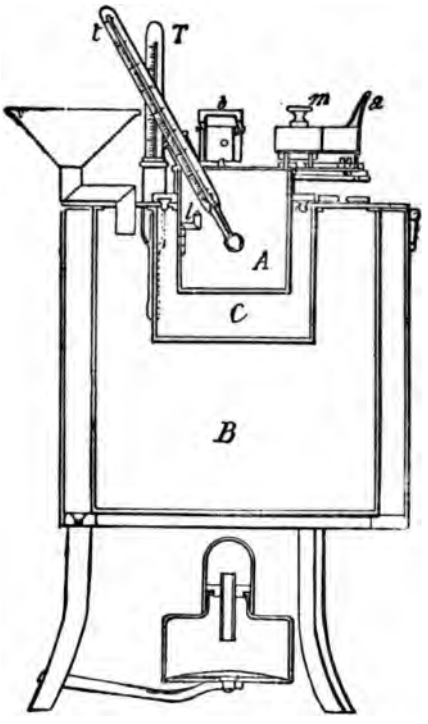


FIG. 44

The vessel *A* is heated by a water bath *B*, the intermediate space *C* being left empty, and is supported on an ebonite ring fixed to the bath *B*. The latter contains a thermometer *T* with a red mark at 55°. The bath is first heated to this temperature, the covered vessel containing the oil up to the prescribed level being fitted and the thermometer *t* in the oil read. For each rise of temperature of 0·5° the clockwork mechanism is operated, the test being repeated until the flame causes a small explosion: the temperature then shown is the flash point and should be corrected for the pressure (± 0·035° per 1 mm. below or above 760 mm.), the result being returned to the nearest half-degree.

The dimensions of all parts of the apparatus are exactly controlled and with careful working the results should not vary by more than 0·5-1° at the most.

**5. Temperature of Ignition.**—When the flash point has been measured, the cover of the vessel *A* is removed and a thermometer supported in the oil, the heating being continued and, after each 1° rise, a flame brought near the surface of the liquid without touching it. When the oil fires, the temperature is observed, the thermometer immediately withdrawn and the oil extinguished with an asbestos card.

**6. Determination of the Viscosity.**—This is not usually carried out with illuminating oil, but it may, if required, be effected as in heavy oils (*q.v.*, Physical Tests, 7) or, more exactly, by means of the Ubbelohde viscometer.[1]

[1] *Petroleum*, 1909, IV, p. 861.

**7. Determination of the Illuminating Power.**—This requires a *photometer*, one of those most largely used being that of Lummer and Brodhun (Fig. 45), which is an improved form of the Bunsen type. It consists

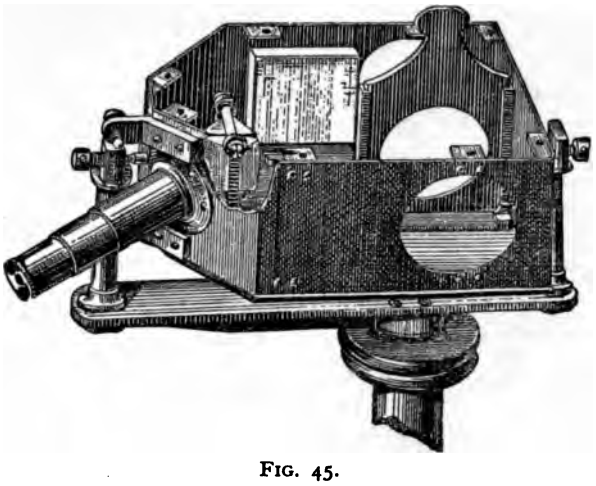

FIG. 45.

of a closed chamber with two opposite circular apertures, by means of which the two faces of a white screen in the chamber are illuminated respectively by the lamp to be examined and by a lamp chosen as unit. The two faces of the screen reflect the light, by means of a system of lenses, on to two concentric zones of the field of the telescope eye-piece shown to the left of the figure. When the screen is equally illuminated on both faces, the two zones of the field appear exactly similar. The two sources of light are placed at the extremities of a double guide 3 metres in length and graduated in half-centimetres—the *photometric bench*. The position of the photometer is adjusted between the lights so that the field is uniformly illuminated: the intensities of the two lights are then proportional to the squares of their respective distances from the screen of the photometer.

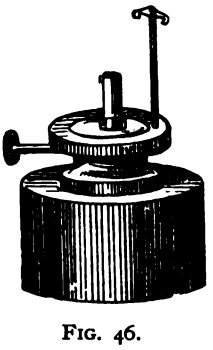

FIG. 46.

Photometric observations are made in a dark room with blackened walls, with a temperature about constant and no sensible air currents. The standard lamp used is the Hefner amyl acetate lamp with a flame 4 cm. high (Fig. 46).

The values obtained with other types of lamp still in use in different countries may be converted into those given by the Hefner lamp by means of the factors given in the following table [1]:

[1] Uppenborn and Monasch: *Lehrbuch der Photometrie*, Munich and Berlin, 1912.

TABLE XLI

| Unit. | Hefner Candle. | International Candle, Decimal Candle (Normal Candle), American Candle, Pentane Candle. | Carcel. |
|---|---|---|---|
| Hefner candle . . . . | 1 | 0·9 | 0·093 |
| International candle, decimal candle (normal candle, American candle, pentane candle . . . . . | 1·11 | 1 | 0·1035 |
| Carcel . . . . . | 10·75 | 9·65 | 1 |

The petroleum to be tested is poured into a lamp and the latter weighed, centred on the photometric bench and lighted, the time being noted. The flame is kept low at first and is then gradually raised until it is as large as possible without smoking and without the wick charring excessively. Photometric observations are then begun and are repeated at regular intervals —the time of each being noted—until the oil is almost exhausted, the wick not being further moved; the lamp is finally extinguished and weighed, the consumption of oil being thus ascertained.

The position of the Hefner lamp is taken as the zero of the scale and that of the oil lamp as 300 cm.; the illuminating power of the lamp is then given by the formula,

$$i = \left(\frac{l - x}{x}\right)^2$$

where $i$ is the intensity required, expressed in candles (Hefner), $l$ the length of the photometric bench and $x$ the distance of the photometer screen from the zero point of the scale. The mean of the different observations gives the mean intensity in candles.

The mean consumption per candle-hour is the quotient of the total weight of oil used by the total candle-hours, and the yield, that is the amount of light (in candle-hours) produced per gram of oil, the quotient of the total candle-hours by the weight of oil consumed.

It is necessary also to take account of the variation of the luminous intensity during the experiment. As a rule, after reaching its maximum a few minutes subsequent to the lighting of the lamp, it diminishes more or less slowly to the end, mainly on account of the carbon ring formed at the summit of the wick in consequence of the incomplete combustion of the heavier fractions, this hindering the rise of the oil into the flame. This decrease is expressed by a fraction, the numerator of which is the difference between the maximal luminous intensity reached soon after the beginning and that observed just before the exhaustion of the oil, and the numerator the maximal intensity.

EXAMPLE: During 5 hours the following intensities were observed, the consumption of oil being 180 grams.

| Time. | Luminous intensity in candles. |
|---|---|
| 1st hour | 9·50 |
| 2nd ,, | 9·00 |
| 3rd ,, | 8·50 |
| 4th ,, | 8·00 |
| 5th ,, | 7·50 |
| Total candles | 42·50 |

Mean luminous intensity = 42·50 : 5 = 8·50 candles.
Mean consumption per candle-hour = 180 : 42·50 = 4·23 grams.
Yield, or light produced per gram of oil = 42·50 : 180 = 0·23 candle-hour.
Decrease of luminous intensity = (9·50–7·50) : 9·50 = 0·21.

It must be pointed out that petroleums of different quality do not burn equally well in all lamps, principally on account of the different quantities of air they require to burn completely. If the lamp does not allow access of sufficient air the combustion, being incomplete, will give rise to smoke and unpleasant smell, whereas excess of air in the flame will cool the latter too much and diminish the luminosity as well as the consumption. In general, Russian oils require more air than the American, while with oils from the same locality, more air is required by those rich in heavy and poor in light fractions. In any case it is necessary, to obtain comparable results, to work with the same lamps and to allow for the form and dimensions of their essential parts, namely, the holder, burner and chimney. Marked influence on the course of the combustion is also exercised by the wick, especially the length and quality of the fibre and the structure and compactness of the tissue; wicks of the same quality and dimensions should be used in all measurements, and they should be either new or washed thoroughly with petroleum ether and then dried.

**8. Behaviour at Low Temperature.**—This test is made on oils to be used in the open in cold places. A little of the oil is cooled for an hour, in a test-tube with a thermometer passing through its stopper, at the lowest temperature to which it is likely the oil may be exposed, to ascertain if the oil remains clear and mobile or if solid substances separate. For the procedure, *see* Heavy Oils, Physical Tests, 8.

## 2. Chemical Tests

**1. Acidity.**—This may be due to inorganic acids (principally sulphuric acid) or to organic acids. The tests are made as follows:

(*a*) INORGANIC ACIDS. The oil is shaken with tepid water containing a little methyl orange; if the colour changes to red, the aqueous layer is separated and tested with barium chloride.

(*b*) ORGANIC ACIDS. If test (*a*) gives a positive result, the oil to be used for the present test is first washed with hot water: 100 c.c. of the oil are dissolved in 100 c.c. of a neutral alcohol-ether (1 : 4) mixture in presence of a drop of phenolphthalein solution and a drop of N/10-sodium hydroxide solution, the whole being shaken in a cylinder: the red colour persists if the oil is neutral, but disappears if organic acids are present.

**2. Degree of Refining.**—The oil is shaken with an equal volume of

sulphuric acid (D 1·53) and note made if the latter becomes yellow or brown. If any appreciable coloration occurs, it is desirable to ascertain if any marked rise of temperature takes place.

**3. Determination of the Sulphur.**—This is usually done only with oils having a penetrating and unpleasant odour. The simplest method is that of Heussler and Engler,[1] this consisting in burning the petroleum in a suitable lamp, the chimney of which is joined to a bent tube dipping into 20 c.c. of 5% potassium hydroxide solution made just yellow by bromine and then left in the air to decolorise; the absorption vessel communicates with a pump. The lamp charged with the oil is weighed and lighted, the tube fitted and the suction adjusted so that the combustion is complete and regular. The sulphurous anhydride produced is absorbed and transformed into sulphuric acid by the alkaline bromine solution. After 10–12 grams of the oil are burnt, the flame is extinguished, a little more air drawn through, the lamp again weighed and the sulphuric acid determined as barium sulphate. The caustic potash used and also the air must, of course, be free from sulphur products.

The sulphur may also be determined by the Mahler calorimetric bomb (*see* Crude Petroleum, Chemical Tests, 3).

**4. Distinction between Petroleums from Different Localities.**—This is based mainly on the following tests:

(*a*) SPECIFIC GRAVITY. This is usually 0·780–0·805 for American and 0·820–0·825 for Russian lighting oils.

A better criterion than the specific gravity is furnished by the specific gravities of the fractions obtained on distillation, these differing by about 0·04 for identical boiling points. Thus, the fractions of an American and a Russian petroleum distilling between 230° and 250° have the respective densities 0·798 and 0·841, and the fractions between 250° and 270° the densities 0·809 and 0·850.

(*b*) TREATMENT WITH BROMINE. 2 or 3 c.c. of American petroleum are not coloured when treated with a drop of bromine, whereas other petroleums become coloured under these conditions.

(*c*) SOLUBILITY IN A MIXTURE OF CHLOROFORM AND ALCOHOL. Riche and Halphen[2] have suggested a method based on the different solubilities, in a mixture of chloroform and aqueous alcohol, of fractions of equal specific gravities from American and Russian petroleums. It is carried out as follows: Several successive fractions of the oil are separated by distillation and the specific gravity of each of them determined at 15°. The volume of a mixture in equal volumes of pure anhydrous chloroform and 92·8% alcohol necessary, when run in slowly from a burette with continual shaking, to remove the turbidity produced, is then determined. For the lighter fractions (which have about the same compositions with Russian and American petroleums), the solubility is about the same for the same specific gravities, but for fractions with specific gravities above 0·760, the difference in solubility continually increases. Thus, the corresponding fractions of

[1] *Chem. Zeit.*, 1896, p. 197.

[2] *Journ. de Pharm. et Chim.*, 1894, XXX, p. 289; Rossi: *Ann. Labor. Chim. Gabelle*, 1900, IV, p. 379.

American and Russian petroleums of D 0·780 dissolve respectively in 5·2 and 4·1 c.c. of the solvent, and fractions of D 0·820 in 9·5 and 4·5 c.c. respectively of the solvent.

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A *good lamp oil* should be clear and only slightly coloured (in time, however, darkening occurs if the oil is exposed to the air); its odour should be neither too penetrating nor unpleasant, as this would indicate the presence of sulphur compounds.[1] It should have no appreciable acidity and should not turn brown with sulphuric acid. For use in cold places, it should remain clear and mobile at a temperature lower than that to which it is likely to be exposed. The specific gravity is usually 0·780–0·805 for American and 0·0820–0·825 for Russian oils.

With regard to *fractional distillation*, a good oil should not begin to distil below 110° and should contain only small amounts of light and heavy oils. The limits usually demanded for ordinary lamp oils are 5% of light oils and 10% of heavy oils, but the proportions actually present are well within these limits for good oils. As regards the fractions comprised between 150° and 300°, there should be no great disproportion between the amounts of these and the middle fractions should predominate over the extreme.

The *flash point* is of importance as an indication of the danger attending the use of the oil. In Italy, legislation demands that the flash point for lamp oil, determined by the Abel-Pensky apparatus, should not be below 21° C.

The *viscosity* of lamp oil, measured by the Engler apparatus at 20° C., is 1–1·05, or, measured by the Ubbelohde apparatus, 1·10–1·80, and is usually somewhat lower for Russian than for American oils.

The *illuminating power* varies with the lamp used, but, under ordinary conditions, the consumption per candle-hour at 15–20° varies from 3·5 to 5 grams. The decrease in luminosity from the beginning to the end of the combustion is generally greater with American than with Russian petroleums. The latter burn with a less initial and greater final luminosity than the former. In any case, with a good oil the decrease should not exceed one-fourth of the initial value.

Lamp oils from crude petroleums rich in solid paraffin, e.g., those from Boryslav, Pennsylvania, etc., if not properly prepared, deposit *solid paraffin* at — 10°, but those of Russian origin remain clear even at — 20°.

The *calorific power* of lighting oil is 11,000–12,000 cals.

## MIDDLE OILS

### (Gas Oils)

These are intermediate in character to lighting oil and heavy oils. They are mobile and yellow to dark brownish-yellow, their density being between about 0·845–0·855, their b.pt. 300–350°, and their viscosity below 3 (Engler).

The most important determination with these oils is the yield of gas and the calorific value of the latter. The amount of gas given is determined in a small works plant. In the laboratory it may be ascertained approximately, in comparison with a typical oil, in Ross and Leather's apparatus,[2]

[1] According to Kissling and Engler (*Chem. Rev. Fett. Ind.*, 1906, p. 158), the proportion of sulphur in Russian petroleums lies between 0·027 and 0·030%; in Galician, between 0·039 and 0·062%; in Pennsylvanian, between 0·027 and 0·029%, and in those from Ohio, between 0·04 and 0·5%. A good oil should not contain more than 0·03%.

[2] *Journal of Gaslighting*, 1906, p. 825.

consisting of a retort (23 × 14·5 × 12 cm.) in which 15 c.c. of the oil are gasified. The temperature of gasification is measured with a pyrometer and the volume of gas produced and the components absorbable by fuming sulphuric acid determined.

Another apparatus for this purpose has been proposed by Wernecke and modified by Hempel.[1] The results obtained on the laboratory scale are, however, not accurate, the best method being the works test.

The following determinations may also be required: Specific gravity, behaviour on distillation, flash point, viscosity, calorific power and sulphur, these being carried out as indicated in the articles dealing with *crude petroleum* and *heavy oils*.

*Middle* or *gas oils* are used for making illuminating gas, for carburetting water gas, as a motive force, as a cleaning oil, and also as solvent.[2]

The yields from 1 kilo of oil vary between the following limits: gas, 500–600 litres; tar, 300–400 grams; coke, 40–60 grams.

## HEAVY OILS

## (Lubricating Oils)

These oils vary somewhat in colour, appearance and consistency. The colour is usually reddish, brown or blackish, and marked fluorescence is also observed; some such oils are, however, colourless or yellowish and not at all or but slightly fluorescent (vaseline oil). The smell is similar to that of lamp oil if more volatile oils are present, but very heavy oils are odourless. A bituminous smell indicates faulty refining and a tarry or resinous odour the presence of extraneous matter. As a rule, these oils are liquid and more or less viscous, but some are highly mobile and others have almost the consistency of fats.

Analysis of lubricating oils aims at ascertaining if their characters are in correspondence with the uses for which they are designed or with the conditions fixed in the purchase contract.

Both physical and chemical tests are made.

### 1. Physical Tests

**1. Colour.**—This is usually compared with that of a selected oil by means of the colorimeter (*see* Lighting Oil) or more simply by observing equally thick layers of the two oils in similar rectangular bottles.

It should be borne in mind that heavy oils may be coloured artificially. Aniline dyes are usually employed for this purpose and may be extracted from the oil by water or dilute alcohol in presence of acid or alkali and characterised by the tests to be given under the heading, Colouring Matters.

The standard colour for the fiscal classification of heavy mineral oils is that of a 0·75% solution of pure, crystallised potassium chromate, this being compared by transmitted light with the oil in question in an equally thick layer.

[1] *Journal für Gasbeleuchtung*, 1910, p. 78.

[2] For this purpose oils of lower density and solar oils from the distillation of shales are also used.

**2. Specific Gravity.**—Determined as with crude petroleum.

**3. Distillation.**—The flasks used for crude petroleum are employed. The temperature at which the distillation commences is noted and the distillate up to 300-310°, representing the light oils and illuminating oil, collected and weighed.

For fiscal purposes (in Italy), the procedure followed is that indicated under *Crude petroleum*, 2. When decomposition occurs, recourse is had to distillation under reduced pressure, as indicated later for residues.

**4. Volatility.**—When heated, heavy oils begin to emit vapour at a certain point. To determine the quantities of the oil evaporating in a certain time at different temperatures, in accordance with the conditions laid down in contracts, the following procedure (Holde) is employed: The oil-container *A* of the Pensky-Martens apparatus (Fig. 47) is charged to the mark with the oil and weighed. It is then heated for the prescribed time; for temperatures between 100° and 200°, a glycerine bath is used, but for higher temperatures (200–300°) a bath of a heavy cylinder oil having a flash point above 300° is employed.

The temperature of the oil is measured by means of a thermometer from which the adhering oil is removed by a piece of filter-paper (previously weighed with the crucible), which is added to the oil. After the experiment, the oil-contained is cooled in water, dried, left in a desiccator for about 30 minutes and weighed; the loss in weight gives the volatile oil.

With temperatures higher than 300°, the oil may be heated directly in the Pensky-Martens apparatus.

**5. Flash Point.**—This is determined for heavy oils in the Pensky-Martens apparatus (Fig. 47). The upper view shows a section of the essential parts of the apparatus. *A* is a brass cylinder similar to that of the Abel apparatus and is fitted with a level gauge and a vaned stirrer *a*; it is placed inside an iron envelope *B* with very thick walls. This part of the apparatus is surrounded and protected from radiation by a cupola-shaped brass mantle and is heated by means of a triple burner *C*, a wire gauze *R* being interposed. The cover of the vessel *A* carries a thermometer *t* usually graduated from about 80° to 250°, with its bulb dipping into the liquid, and a gas flame *f* which is brought near to a small window and the latter at the same time opened by turning a knob *b*. A fixed flame *l* serves to re-light the movable flame when this is extinguished by the explosion. All the dimensions of the apparatus are fixed exactly.

The oil (previously dehydrated with calcium chloride if it contains water) is placed in the vessel *A* and the apparatus heated to 80°, after which the stirrer is started and the flame regulated so that the temperature rises about 5° per minute. Observations are made firstly at intervals of 2°, but when the elongation of the flame indicates the proximity of the flash point, at each degree. The results of several experiments made with the same oil do not as a rule differ by more than 2° or 3° among themselves.

A simpler but less exact method of finding the flash point of a heavy oil consists in heating the latter in a porcelain crucible 4 cm. in height and width, which is filled to within 1 cm. from the top and furnished with a

thermometer. The crucible is heated on a sand-bath so that the temperature rises about 5° per minute, a small flame being brought near to the top of the crucible at regular intervals until a slight explosion occurs.

The results obtained by these two different methods vary in oils of normal composition by 5–40°; the method employed for the determination should always be indicated.

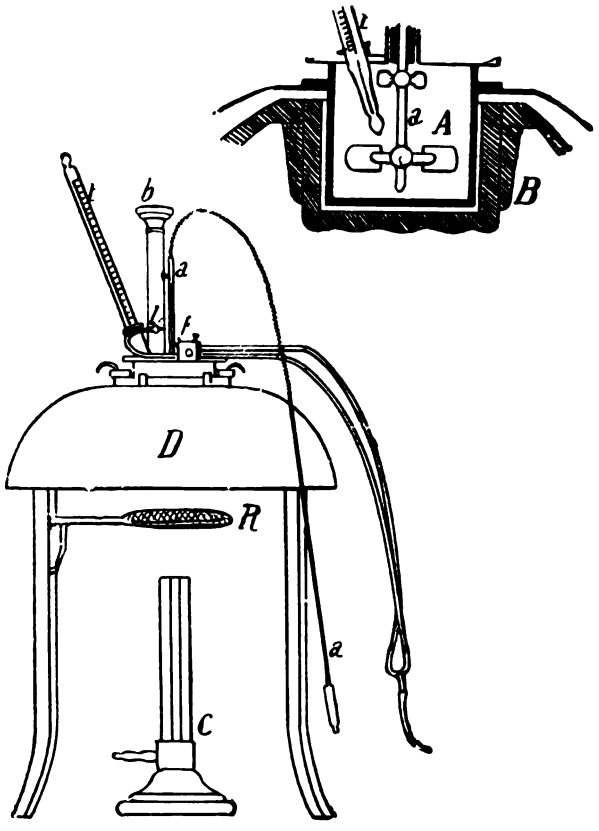


FIG. 47

**6. Temperature of Ignition.**—This determination may be made as the complement of that of the flash point—when an open crucible is employed—by continuing to heat so that the temperature rises from 2° to 6° per minute; a flame is held for 1-2 seconds near the surface of the liquid, the temperature of ignition being taken as that at which the surface of the oil ignites.

The temperature of ignition is usually 20–60° above the flash point.

**7. Viscosity.**—This is determined by means of viscometers, that of Engler (Fig. 48) being the one most used. It consists of a covered cylindrical brass vessel *A*, the slightly sloping base of which is provided with a small central aperture *a* leading to an efflux tube which can be shut by means of a wooden plug *b*. In the vessel *A* are three points marking the level of the liquid. The vessel *A* is surrounded by a larger one, the annular space

between serving as a bath to maintain the temperature constant. Thermometers *c* and *d* give the temperatures in the vessel *A* and in the bath, and the latter is heated by means of a ring burner; the whole is supported on a tripod. Under the efflux tube is a glass flask *C* with marks on the neck at 200 c.c. and 240 c.c. All the parts of the apparatus are of *exactly* standardised form and dimensions.

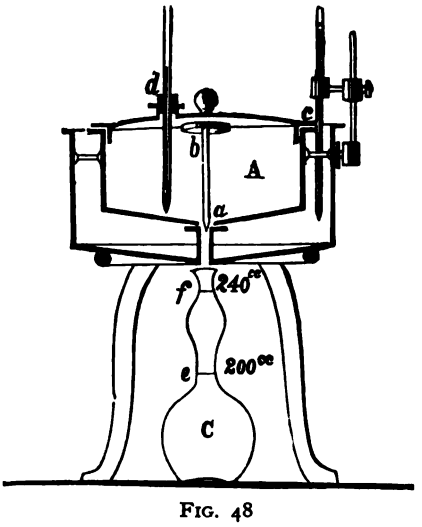

FIG. 48

To make a determination, the internal vessel is filled to the desired level with the oil to be examined (dehydrated by decantation and filtered through cotton wool dried at 100°), the efflux orifice being shut. The outer vessel is then filled with water and heated carefully until the oil reaches the temperature at which the viscosity is to be measured. The flask is then placed underneath and the plug rapidly withdrawn, the time being counted exactly from this instant. The exact time taken to fill the flask to the 200 c.c. mark, divided by that taken under similar conditions, with a standard liquid, gives the viscosity of the oil in Engler degrees.

Usually a temperature of 20° is employed and water taken as the standard, and the apparatus should be controlled from time to time with water; as a rule 52–53 seconds are required for the efflux of 200 c.c. of water.

Between one determination and another of the time of efflux of water, the difference is ± 1·5 second, which corresponds with a difference of ± 3% in the degrees Engler. If, then, the difference in the time of efflux of water is less than 1 sec., as prescribed for the use of the apparatus, the difference in the degrees Engler is ± 2·3%.

Each apparatus is sold duly controlled, the time of efflux for water being indicated.

For very dense heavy oils, and for such semi-solid products as vaseline, the viscosity should be determined at a higher temperature, e.g., 50°, 60°, 100° or, sometimes, 180° or even higher. In the latter cases the whole of the apparatus is placed in a large oven, or use made of an apparatus in which the outer vessel—tightly closed and fitted with a reflux condenser —serves as a vapour-bath in which water (100°), aniline (180°) or other suitable liquid is boiled. In some cases it may be advantageous to determine the viscosity at temperatures below 20°.

Prior to a determination, the apparatus should always be thoroughly cleaned from every trace of oil by washing with benzine or ether and drying with absorbent paper.

The viscosity of heavy oils constitutes an indirect indication of their

*lubricating value*; the latter may be determined directly by means of suitable machines, that of Martens [1] being most commonly employed.

Viscometers of other types are those of Lamansky-Nobel [2] (Russia), Redwood [3] (Great Britain) and Saybolt [4] (America). In France use is made of Barbey's *ixomètre*, which determines the coefficient of fluidity of an oil by measuring the volume of an oil dropping during a certain time.

The ratio between the values of the viscosity found by the Lamansky-Nobel and Engler apparatus respectively is about constant and is 1·13–1·18 for fluid oils and 1·20–1·26 for more viscous oils (engine and cylinder oils), so that number of Engler degrees = number of Lamansky-Nobel degrees divided by such factor.

The relations between Engler values and those obtained with the Redwood and Saybolt apparatus are given by the following formulæ, in which $t_r$ and $t_s$ represent the times of efflux in the two apparatus and $E$ the Engler degrees:

$$(1)\quad t_r = 192{\cdot}2k\left(1 + \sqrt{1 + \frac{0{\cdot}01624}{k^2}}\right)$$

$$(2)\quad t_s = 228{\cdot}7k\left(1 + \sqrt{1 + \frac{0{\cdot}01309}{k^2}}\right)$$

$$(3)\quad k = 0{\cdot}08019E - \frac{0{\cdot}07013}{E}$$

In practice, for viscosities which are not too low (not less than 3 or 4 degrees Engler), it is a sufficiently close approximation to assume that the times of efflux in the Engler, Redwood and Saybolt forms of apparatus (used according to the conditions prescribed for each case) are in the ratios 100 : 59 : 70.

**8. Behaviour at Low Temperature.**—When strongly cooled, lubricating oil first thickens and ultimately congeals and the aim of investigating its behaviour is either to ascertain if the oil remains liquid at a certain temperature or to discover when it begins to thicken without assuming a tallowy consistency.

In the former case a test-tube 15 mm. in diameter is filled to a height of about 3 cm. with the oil and placed, together with a thermometer in a beaker about 12 cm. in height and diameter containing a salt solution of known freezing point [5] corresponding approximately with the temperature at which the oil should remain liquid. The whole is placed in an earthenware vessel and cooled for an hour with a freezing mixture composed of two parts of snow or pounded ice and one part of common salt.[6] The tube is then taken from the solution to see if the oil has remained liquid.

[1] D. Holde: *Untersuchung der Kohlenwasserstofföle und Fette*, Berlin, 1913, p. 158; W. Hinrichsen: *Das Materialprüfungswesen*, Stuttgart, 1912.

[2] Wischinsin and Singer: *Chem. Rev. Fette Industrie*, 1897.

[3] B. Redwood: *Petroleum*, London, 1913.

[4] B. Redwood: *Petroleum*, London, 1913.

[5] For this purpose the following solutions may be used:

| Freezing point. | Composition. |
|---|---|
| − 3° | Water, 100; $KNO_3$, 13 parts. |
| − 4° | ,, 100; $KNO_3$, 13; NaCl, 2. |
| − 5° | ,, 100; $KNO_3$, 13; NaCl, 3·3. |
| − 8·7° | ,, 100; $BaCl_2$, 35·8. |
| − 10° | ,, 100; $CaCl_2$, 22·5. |
| − 14° | ,, 100; $NH_4Cl$, 20. |
| − 15° to − 15·4° | ,, 100; $NH_4Cl$, 25. |

[6] With this mixture, a temperature of − 21° may be attained. For lower temperatures, the two vessels are charged with alcohol which is cooled with solid carbon *dioxide*; constant temperatures of − 25° and − 30° are thus obtained.

In the second case a preliminary test is first made. The oil is placed in a test-tube through the stopper of which passes a thermometer, and cooled in a freezing mixture ; from time to time the tube is withdrawn for an instant and inclined, so that the temperature at which the oil begins to solidify may be discovered. A saline solution with a freezing point a little lower than this temperature is then chosen and the oil kept in the apparatus referred to above at the temperature found in the preliminary trial. At the end of the time the test-tube is removed from the solution and inclined so that an idea may be obtained of the degree of thickening ; the latter may also be estimated by noting the adhesion of the oil to a glass rod when this is withdrawn.

Supercooling of the salt solution is avoided by scraping the congealed parts from the walls of the containing vessel or by withdrawing the vessel itself for an instant from the freezing mixture.

If the cooled oil is heated and another examination made of the behaviour at low temperatures, the result may be different from that of the first test; such difference may be due to the variations of temperature to which the oil is subjected during transport and storage. It is therefore useful to carry out the test on the oil, first as received and then after it has been heated to 50° for ten minutes and subsequently cooled for 30 minutes in a water-bath at 20°. With mixtures of mineral and fatty oils, the cooling should be protracted for 4–10 hours, one test being made without stirring the oil and the other with stirring every 15 minutes.

**9. Test of Fluidity at Low Temperatures.**—This is effected when required by pipetting the oil into a U-tube of definite diameter (usually 6 mm.), cooling the latter in a cooling mixture, and then measuring the change of level produced by applying at one side, for a definite period (generally 1 minute), a known pressure, e.g., 50 mm. of water, by means of a water manometer. The number of mm. measuring the change of level represents the degree of fluidity of the oil at the temperature of the experiment.

## 2. Chemical Tests

**1. Detection of Water and Solid Substances.**—These are usually recognised by the appearance and are investigated as with crude petroleum. Water may also be detected by heating the oil in a test-tube for about 15 minutes : if water is present froth is formed and drops of water appear in the cold part of the tube.

**2. Determination of the Acidity.**—Acidity is due either to mineral acids (sulphuric acid) introduced during refining or to organic acids.

(*a*) Acidity due to mineral acids may be detected by shaking 50–100 grams of the oil with double the quantity of distilled water, allowing the aqueous layer to separate, filtering it through a moist filter-paper and testing about 30 c.c. of the filtrate with a few drops of methyl orange solution (0·03%) : when mineral acid is present a red coloration is obtained.

(*b*) The acidity due to organic acid is determined differently according as the oil is pale or dark.[1]

[1] When the test for inorganic acidity made as in (*a*) gives a positive result, the oil should be first subjected to washing with hot water.

With a pale oil, 10 grams are dissolved in about 150 c.c. of a perfectly neutral mixture of ether (4 parts) and alcohol (1 part) and the solution titrated with decinormal alcoholic sodium hydroxide in presence of phenolphthalein. If the colour of the oil is too intense to admit of observation of the colour change of phenolphthalein, 10 grams of it are shaken with 100 c.c. of absolute alcohol and 50 c.c. of the separated alcoholic layer titrated with decinormal alcoholic caustic soda in presence of phenolphthalein.[1]

The acidity is expressed as sulphuric anhydride or oleic acid, or as the number of milligrams of potassium hydroxide necessary to neutralise 1 gram of the oil, the last being termed the *acidity number* of the oil; 1% $SO_3 = 7{\cdot}05\%$ oleic acid = acidity number of 14.

**3. Alkalinity.**—This is detected by adding phenolphthalein to another aliquot part of the water with which the oil was shaken in the determination of the mineral acids; with free alkali a red coloration is obtained.

It must be borne in mind that, if the oil in question contains alkali soaps, the alkalinity found may be due to partial decomposition (hydrolysis) of the soap by water.

**4. Determination of the Solid Paraffin and Asphalt.**—As in crude petroleum (*q.v.*, Chemical Tests, 4 and 5).

**5. Detection of Oils, Fats and Waxes.**—(1) QUALITATIVE. 5 c.c. of the mineral oil are heated for about 15 minutes in a test-tube with a stick of caustic soda weighing about 4 grams, either over a naked flame or, better, in a paraffin bath at 200–210°. If fatty substances are present, even only to the extent of 1–2%, the whole mass becomes solid and gelatinous on cooling.

(2) QUANTITATIVE. If the qualitative test gives a positive result, the quantitative estimation may be carried out as follows:

(*a*) By the saponification number determined as indicated for fatty substances; about 5 grams of substance are used and, besides alcoholic potash, an equal quantity of benzene is added, the heating in a reflux apparatus being continued for about an hour. The saponification number thus obtained is divided by 1·85, the result being the percentage of fatty substances calculated from the mean value of their saponification number.

In presence of wool fat or waxes—which are usually detectable by the odour and consistency—the results obtained are inaccurate, since these substances have saponification numbers different from those of fatty substances.

(*b*) By direct weighing, according to the directions given by Armani and Rodano[2]:

5 grams of the oil are saponified in a flask with alcoholic potash solution (12 grams of caustic potash in 100 of alcohol), the flask being immersed in a bath of boiling water. As reflux apparatus, a simple funnel is placed in the mouth of the flask, so that a large part of the alcohol is

[1] According to H. Loebell (*Chem. Zeit.*, 1911, 35, p. 276), the acidity is determined in 10 c.c. of the oil, using an alcohol-benzene mixture (1 : 2) as solvent, alkali blue as indicator and decinormal alcoholic caustic soda as standard solution.

[2] *Industria saponiera*, Milan, 1912, p. 169; *Ann. Lab. chim. centrale Gabelle*, Vol. VII, p. 278.

lost by evaporation; sufficient, however, remains for the saponification, which takes place fairly rapidly (in about half an hour).

Without evaporating off all the alcohol, the contents of the flask are poured into a separator and the flask thoroughly rinsed out, at first with small quantities of alcohol and then with ether. Sufficient water is added to dissolve the soap formed and sufficient ether to dissolve the mineral oil. The alkaline liquid is almost neutralised towards phenolphthalein by means of acetic acid and shaken, a sharp division occurring on standing between the ethereal layer containing the mineral oil and the soap solution. The ethereal liquid is separated, washed with distilled water until the alkaline reaction disappears, and distilled from a tared flask, the last traces of ether being expelled in a current of air.

The residue is dried in an air-oven at 105° for an hour and weighed; the weight is multiplied by 20 and the product subtracted from 100, the remainder being the percentage by weight of the fatty substance.

To determine the nature of the fatty matter, the soap solution is treated with dilute sulphuric acid and the fatty acids collected and identified by their colour reactions and their physical characters (*see* chapter on Fatty Substances). If blown or oxidised oils have been added to the mineral oil, the fatty acids are brown, have an odour of vegetable oils and are soluble in ether, from which they are partially precipitated by petroleum ether; the precipitated part has a pitchy appearance. In some of their characters, these fatty acids might be confused with those of fish oils, but the latter have a quite different odour and are precipitated by Halphen's bromine reagent (*see* Fish Oils), with which the fatty acids of oxidised oils give no precipitate.

When it is necessary to examine the characters of mineral oil changed by previous operations, the saponification is carried out in the cold as follows:

In a separating funnel, 50 grams of the oil, 200 c.c. of light petroleum ether and 200 c.c. of 10% alcoholic potash (in 95% alcohol) are vigorously and frequently shaken for about four hours and then allowed to settle, the ethereal layer being separated and washed several times by shaking with cold water, and the petroleum ether evaporated on a water-bath. The residue consists of the mineral oil; its freedom from fatty matter may be ascertained by determining its saponification number, which should be almost zero.

**6. Detection of Alkaline and Alkaline-Earthy Soaps.**—1. QUALITATIVE. The alkaline soaps may be dissolved by shaking the oil with water, whilst the alkaline-earthy soaps are decomposed by shaking with hydrochloric acid: in this way the bases pass into solution in the hydrochloric acid.

2. QUANTITATIVE DETERMINATION. About 10 grams of the oil are weighed, dissolved in 50 c.c. of ether, and shaken in a separating funnel with dilute hydrochloric acid, the ethereal solution being allowed to separate and washed repeatedly with water; if the oil is sufficiently clear, alcohol is added and the acidity determined, the fatty acids being deduced from the result obtained (*see* Fatty Substances). If, however, the oil is too

highly coloured for direct titration, the ether is distilled off, the residue treated with 20 c.c. of hot alcohol and the acidity of the alcoholic liquid determined. Examination of the aqueous hydrochloric solution will indicate the base present in the soap.

**7. Resin Oils.**—1. DETECTION. Resin oils are detected by their odour and by Morawski's reaction, which consists in treating a small quantity of the oil in a test-tube with acetic anhydride and adding a drop of sulphuric acid (D 1·53) : the appearance of a transient violet coloration indicates the presence of resin oil.

Resin oils may be detected also by shaking the oil (freed, if necessary, from saponifiable matter) with an equal volume of acetone and allowing the two liquids to separate, the acetone containing very little mineral oil and almost the whole of the resin oil. If the solvent is evaporated, the resin oil in the residue may be characterised by the red coloration which it imparts to an equal volume of sulphuric acid (D 1·6), by its high specific gravity (0·970–0·980) and by its rotatory power.

2. DETERMINATION. Storch's method is used: 10 grams of the oil (freed from saponifiable matters when these are present) are treated in a flask, at a gentle heat and with shaking, with 50 grams of 96% alcohol. After cooling, the alcoholic liquid is transferred to a weighed beaker and the oily liquid washed with a little alcohol, which is also added to the beaker. The alcohol is evaporated on the water-bath and the residue weighed ($A$). This residue is treated again with alcohol (10 times its weight), evaporation of the alcoholic solution giving a new residue ($B$). The mineral oil present in this residue is calculated by means of the formula, $\frac{(A-B)b}{(a-b)}$, where $A$ and $B$ are the weights of the two residues and $a$ and $b$ the quantities of alcohol used in their treatment. Subtraction of the calculated weight of mineral oil from $B$ gives the quantity of resin oil.

EXAMPLE : 10 grams of oil, treated with 50 grams of alcohol, gave a residue of 1·51 gram ($A$), and this, treated with 15·1 grams of alcohol, gave a residue, 1·15 gram ($B$). From the proportion

$$50-15\cdot1 : 1\cdot51-1\cdot15 = 15\cdot1 : x,$$

$x = 0\cdot155$. Amount of resin oil in 10 grams of the oil taken $= 1\cdot15 - 0\cdot155 = 0\cdot995$ gram.

**8. Tar Oils.**—The presence of tar oils is recognised besides, by their characteristic odour, by the property they exhibit of reacting energetically with nitric acid (D 1·45) giving nitro-derivatives, by their solubility in conc. sulphuric acid on a water-bath with formation of compounds soluble in water, and by the general reactions of the phenols (*see* Tar Oils, Carbolic Acid).

**9. Defluorescent and Odoriferous Substances.**—To destroy the fluorescence of heavy oils, $\alpha$-nitronaphthalene is usually employed, while the unpleasant fatty smell is masked by addition of nitrobenzene. The latter is readily detected by the odour of bitter almonds it imparts to the oil, whilst the odourless nitronaphthalene is recognised as follows: Holde proposes a preliminary test by heating 1–2 c.c. of the oil for a short time

(0·5–1·5 minute) with 2–3 c.c. of approximately 2N-alcoholic potash: in presence of nitro-derivatives, a blood-red or violet-red coloration appears. To identify the α-nitronaphthalene, the following method (Leonard) [1] is used:

A small quantity of the oil is gently heated with zinc dust and dilute hydrochloric acid with occasional shaking. In this way any α-nitronaphthalene is converted into α-naphthylamine, recognisable by its characteristic disgusting odour. The acid liquid is separated by means of a separating funnel, rendered alkaline with soda and extracted with ether, the ethereal solution being evaporated and the residue taken up in a little alcohol and treated with a drop of sodium nitrite solution acidified with acetic acid: the appearance of a yellow coloration changing to crimson indicates the presence of α-naphthylamine.

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*Heavy mineral oils* have a specific gravity usually between 0·840 and 0·930, although occasionally the value 0·960 is attained. They should not contain any marked quantity of oils distilling below 300° and their flash point should not be below the specified limit laid down in relation to the purpose for which they are to be used. Usually this temperature is above, and often greatly above, 140°. Heavy oils are classified into numerous types having the following characters:

*Light oils for engines, gearing, motors and dynamos*, viscosity mostly 13–25 (at 20°) and flash point 180–220°.

*Spindle oil*, very fluid, viscosity 3·5–15 (at 20°), flash point 160–200°.

*Oils for compressors and refrigerating machines*, still more fluid than the preceding, viscosity 5–7 (at 20°), flash point 140–180°; the solidification point should be below — 20°.

*Automobile oils (cylinder)*, viscosity varying according to the season from 20 to 85 (at 20°), flash point 185–215°.

*Pale heavy oils for engines and gearing*, viscosity 25–45 or more (at 20°) flash point 190–220°.

*Dark heavy oils for locomotives and railway wagons*, viscosity 25–60 (at 20°) and consistency varying with the season.

*Cylinder oils for steam engines*, boiling point high, very viscous (23–60 at 50°), moderately thick, flash point 240–315°, or, for some qualities, 350° or higher. These oils are divided further into low and high pressure cylinder oils.

Another type of heavy oil is that used for electric *transformers*. This should not contain water or mineral acids (reaction neutral) and should be non-volatile; when heated at 100° for some hours it should not decompose (in particular, it should not give solid products or become acid); it should retain sufficient fluidity at — 15° and should have a high flash point. The following requirements should be satisfied by such an oil: viscosity at 20°, 9·8 (Engler); specific gravity, 0·8825; flash point (Pensky), 185°; volatility, determined by heating the oil for 5 hours at 100°, should not exceed 0·06%, or determined by heating for 2 hours at 170°, should not exceed 1%.

All the oils indicated above are subdivided into numerous types indicated by numbers or letters or are sold as special brands.

Oils to be used in the open air or in cold localities should not become turbid or solidify at a temperature somewhat below the minimum to which they may be exposed. As a rule American oils solidify at 0° or a little below, whilst those from Russia do not solidify above — 10° or — 20° or even lower.

[1] *Chem. News*, 1893, p. 297.

Pale refined oils are generally free from acidity or contain only traces (0·03% as sulphuric acid). In dark oils, the acidity may reach 0·3% or, in exceptional cases, 0·5%, but usually it does not exceed 0·15%. Mineral acids should not be present.

## RESIDUES

The bituminous and pitchy residues from the distillation of mineral oils (mazut, astatki or ostatki) are blackish, only slightly transparent, of varying consistency, and of characteristic bituminous odour due to decomposition products of difficultly volatile hydrocarbons.

The determinations and tests usually made are those of water, specific gravity, distillation, flash and ignition points, viscosity, solid paraffin, pitch and asphalt, the methods described for heavy oils being employed; the calorific power and the sulphur are determined as in crude petroleum.

As regards *distillation*, these residues often decompose at high temperatures with formation of more volatile products, so that distillation by the methods already indicated may yield an amount of distillate greater than the true value. This inconvenience is obviated by distilling 100 grams of the oil at reduced pressure (about 30 mm.)[1] from a half-litre flask with a side-tube connected with a sloping condenser, the lower end of which passes through a cork in the neck of a distilling flask similar to that used for the distillation of crude petroleum and having its side-tube in communication with an ordinary water pump. The distillation is continued until the thermometer marks 220°, the distillate being collected in the second flask; at the end of the operation, air is allowed into the apparatus and the flask containing the distillate detached, the residue being then distilled up to 300–310° at the ordinary pressure.

In determining the *flash point*, the residues often froth up at a temperature near 100° and overflow the vessel. In such cases the oil should be dehydrated as indicated for heavy oils. Extinction of the flame at about 100° may be caused by residual traces of water in the product.

When the residues are to be used as fuel, the essential determinations are those of the calorific power and sulphur; the calorific value is about 10,000 calories.

## VASELINE

*Vaselines* of two sorts are sold: the *natural* ones, which consist of hydrocarbons semi-solid at the ordinary temperature, have colours varying from white to yellowish-brown, exhibit slight fluorescence and are translucent, somewhat sticky and ropy; and the *artificial* ones, which consist of solutions of solid hydrocarbons (paraffin wax or ceresine) in paraffin oil and are usually white—sometimes, however, yellow or more or less brown—non-fluorescent, opaque, not sticky and somewhat granular and readily separate paraffin oil at a low temperature.

The examination of vaseline aims at ascertaining its quality and degree

[1] Nasini and Villavecchia: *Relazione sulle analisi e sulle ricerche eseguite nel Lab. chim. Centrale delle Gabelle*, Rome, 1890, pp. 104–106.

of purity, and whether it is natural or artificial. The tests made are as follows:

1. **Suspended Impurities.**—These are recognised by their appearance and are separated by fusing the product and filtering it in an oven.

2. **Mineral Matter.**—From 0·5 to 1 gram is burnt in a platinum dish to ascertain if anyweighable residue remains. Any emission of odours of resin or of burnt fats during the combustion should be noted.

3. **Solubility in Alcohol. Reaction.**—One volume of the vaseline is shaken with two volumes of alcohol, the latter being separated and tested as to acidity or alkalinity and diluted with water to see if it becomes turbid.

4. **Behaviour towards Sulphuric Acid.**—10 grams of the melted vaseline are heated with 2·5 c.c. of a mixture of 5 parts of water with 15 parts of conc. sulphuric acid on a water-bath for 15 minutes, with frequent shaking, any browning of the acid or vaseline being noted.

5. **Detection of Fats.**—2 grams of the vaseline are boiled with a few c.c. of caustic soda solution, the cold aqueous layer being subsequently filtered off and acidified with hydrochloric acid: turbidity or separation of solid substance indicates the presence of fats.

6. **Detection of Resins.**—By Morawski's reaction (*see* Heavy Oils, Chemical Tests, 7).

7. **Viscosity.**—By means of Engler's viscometer (*see* Heavy Oils, Physical Tests, 7), working at 60° C. and keeping also the vessel into which the liquid flows hot.

8. **Determination of the Paraffin Wax.**—In a thin-walled, glass cylinder, 20 cm. tall and 3·5 cm. wide, a weighed quantity of about 0·5 gram of the vaseline is dissolved in the hot in 3 c.c. of ether, and the solution treated with 50 c.c. of 98% alcohol. After being cooled to 0° for an hour and filtered through a filter also kept at 0°, washing with a total quantity of 150 c.c. of 98% alcohol maintained at 0° (*see* Figure, p. 338), the insoluble residue is dissolved on the filter in hot benzene and the solution evaporated in a tared glass dish and the residue weighed. If the precipitate formed in the tube by addition of alcohol to the ethereal vaseline solution is not readily detached from the glass (as happens especially with natural vaselines and with those containing ceresine), the adherent part should be dissolved in benzene and this solution added to that previously obtained.

***

*Pure vaseline* should melt to a clear liquid and should not contain mineral matter, or dissolve appreciably in cold alcohol, or exhibit an acid or alkaline reaction, or turn sulphuric acid brown. According to the Italian Pharmacopœia, pure vaseline for pharmaceutical use should be perfectly neutral and quite free from fats, and should leave no ash.

*Natural* vaselines have viscosities varying from 4·5 to 7·5 at 60° C. (referred to that of water at 20° C. and determined with the Engler apparatus), whilst the viscosity of *artificial* vaselines is usually little above 1 and that of mixtures of natural and artificial vaselines rarely reaches 3·5. Natural vaselines contain 63–80% of solid paraffin insoluble in alcohol, whilst the artificial ones contain only 11–35%, and mixtures of the two intermediate proportions. Ethereal solutions of natural vaselines are precipitated by alcohol in the form of a sticky, cheesy mass, the liquid remaining turbid; with artificial vaselines, a flocculent precipitate is formed, while the liquid remains clear.

## PARAFFIN WAX

*Crude paraffin wax* is coloured more or less intense yellow or brown, whilst the *refined* product is a white or faintly yellow, translucent solid. The following tests are made:

**1. Suspended Impurities. Reaction. Behaviour towards Sulphuric Acid.**—As with vaseline (*q.v.*, 1, 3 and 4).

**2. Melting and Solidifying Points.**—The melting point is determined as with fats, use being made of a capillary tube blown in the middle to a bulb and with the lower end bent upwards after the substance has been introduced (*see* Fatty Substances, 4).

The solidifying point is determined with the Shukoff apparatus (Fig. 49),[1] consisting of a wide-mouthed bottle in which is fixed, by means of a stopper, a tube of the dimensions and form shown. Through the stopper of this tube there passes a thermometer reading to 0·1°.

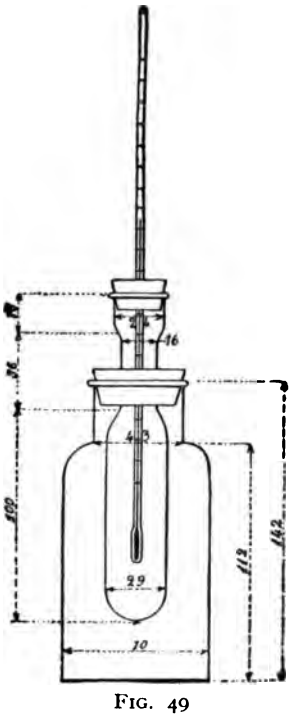

FIG. 49

In the inner tube 30–40 grams of the product are melted, and when the temperature of the fused mass is about 5° above the solidifying point, the apparatus is shaken vigorously and regularly until the contents have become distinctly turbid and opaque. The shaking is then discontinued and the thermometer observed.

The solidifying point is taken as the temperature at which the thermometer remains stationary during the cooling of the fused paraffin, or as the maximum temperature to which it rises after a short arrest in the fall. When no large amount of stearic acid is present, only the temperature at which the mercury remains stationary is observed.

**3. Determination of the Paraffin Wax** (in the crude product).—This is effected by Holde's method. From 0·5 to 1 gram of the substance is dissolved in the necessary quantity of ether, an equal volume of absolute alcohol being added and the liquid cooled to −20°, the subsequent procedure being as described for crude petroleum (Chemical Tests, 4). The percentage found is increased by 1, to correct for the amount dissolved in the solvents.

With soft paraffin waxes this method gives less exact although comparative results.

**4. Detection of Resins and Fatty Acids.**—Of the presence of admixed colophony or stearic acid, an indication is obtained from the acid number, which is zero for pure paraffin wax. If the product exhibits an acid number, 5–10 grams of it, finely chopped, are digested, with frequent shaking, in the

[1] *Chem. Zeit.*, 1901, p. 1111.

cold with about 200 c.c. of approximately 95% alcohol; the liquid is filtered, the alcohol evaporated off and the residue examined. A yellow or brown colour indicates the probable presence of resin, recognisable by the reactions given for heavy oils (Chemical Tests, 7); a white residue probably consists of stearic acid. In any case the nature of the residue may be ascertained by determining the acid and saponification numbers.

**5. Detection of Carnauba Wax.**—This is often added in small proportion to paraffin wax to raise its melting point. Indications of its presence are given by the characteristic aromatic odour and by the saponification number (zero for pure paraffin wax). When, therefore, the product has a saponification number, it is tested for carnauba wax, the following method being employed: 10 grams of the wax, chopped as finely as possible, are digested for some hours with about 500 c.c. of ether, with frequent shaking. After filtration, the insoluble residue—in which the carnauba wax is concentrated—is washed with ether, pressed between absorbent paper and left in the air to dry. The saponification number is then determined and, in presence of carnauba wax, is markedly higher than that of the original substance. In doubtful cases the residue may be again treated with ether, so as to obtain a residue still richer in carnauba wax.

The melting point of the insoluble residue is also determined, this being considerably higher than that of the original material if carnauba wax is present. Finally, the carnauba wax may be identified by decomposing the soap obtained by means of an acid and determining the melting point of the separated fatty acids.

**6. Detection of Coal-tar Colours.**—Any colour in the paraffin wax indicates that a coal-tar colour may be present. To confirm this, the product is extracted with alcohol and the solution tested as usual (*see* Coal-Tar Colours).

***

*Refined paraffin wax* should be white or only faintly yellow, neutral and free from suspended impurities, and should not render sulphuric acid appreciably brown. The melting point varies somewhat: ordinary hard paraffin waxes usually melt at 50–60°, whilst soft ones melt below 50° and in some cases at 30°. On the other hand, paraffin wax melting considerably above 60°, like that from Java, is occasionally found, but in general a product melting below 60° may be regarded as a paraffin wax, and one melting between 60° and 66° as a mixture of paraffin wax and ceresine (*see* later). Such limits are not valid if carnauba wax is present, 5% of this sufficing to raise the melting point by several degrees.

## CERESINE

*Ozokerite* (crude ceresine) is dark yellow or brown, but ceresine itself is white or only faintly yellow, opaque and similar in appearance to white wax. The following tests are made:

**1. Suspended Impurities. Reaction. Behaviour towards Sulphuric Acid.**—As in Vaseline (*q.v.*, 1, 3 and 4).

**2. Melting and Solidifying Points.**—*See* Paraffin Wax, 2.

**3. Detection and Determination of the Paraffin Wax.**—(*a*) Micro-

SCOPIC DETECTION. This is effected by treating a little of the substance with hot alcohol, allowing to cool, filtering, and evaporating a few drops of the filtrate on a slide. A crystalline appearance of the residue under the microscope indicates the presence of a considerable proportion of paraffin wax.

FIG. 50

(*b*) DETECTION AND DETERMINATION BY MEANS OF SOLVENTS (by *Armani* and *Rodano's* method) [1]: This method is based on the different solubilities of paraffin wax and ceresine in a mixture of absolute alcohol and benzene in equal proportions.

Use is made of the apparatus represented in Fig. 50 and consisting of a simple test-tube closed by a stopper channelled to admit air and with a thermometer divided to 0·5° passing through it; the tube is surrounded by a second larger one and by a glass cylinder on a foot. The test-tube containing 0·1 gram of the product is dissolved in 10 c.c. of the hot solvent, is placed in position and allowed to cool slowly, the temperature being noted at which the precipitation of the dissolved substance takes place; this is shown by the appearance of either a turbidity or, with pure paraffin wax or ceresine, a slight crystalline layer. Since there is a difference of 25° between the temperature of precipitation of paraffin wax (25°) and that of ceresine (50°), the presence of even small proportions of paraffin wax may be ascertained, while the percentage may be estimated approximately by means of the following table:

| Paraffin Wax. % | Ceresine % | Temperature of Precipitation. | Paraffin Wax. % | Ceresine. % | Temperature of Precipitation. |
|---|---|---|---|---|---|
| 0 | 100 | 50° | 70 | 30 | 40° |
| 10 | 90 | 48 | 75 | 25 | 38 |
| 20 | 80 | 47·5 | 80 | 20 | 36·5 |
| 30 | 70 | 47 | 90 | 10 | 30 |
| 40 | 60 | 44·5 | 95 | 5 | 27 |
| 50 | 50 | 43 | 100 | — | 25 |
| 60 | 40 | 41·5 | | | |

**4. Detection of Resins and Fatty Acids.**—*See* Paraffin Wax, 4.

**5. Detection of Carnauba Wax.**—*See* Paraffin Wax, 5.

**6. Detection of Coal-tar Colours.**—*See* Paraffin Wax, 6.

**7. Detection of added Mineral Matter.**—This may be talc, kaolin, gypsum, etc., and is detected by dissolving the product in benzine and examining the residue by the ordinary analytical methods.

***

*Refined ceresine* should be white or faintly yellow, neutral and free from suspended impurities and should not render sulphuric acid appreciably brown.

[1] *Ann. Labor. chim. centrale Gabelle*, Vol. VI, p. 109.

Its melting point lies between 61° and 78°, although occasionally higher. In general a product with m.pt. above 66° is regarded as pure ceresine. Such limits are, however, not valid if the ceresine contains carnauba wax.

## MONTAN WAX

### (Bergwachs)

*Montan wax* is obtained by the treatment of the lignites of Saxony. In its appearance it resembles ozokerite or mineral wax, but in composition it is completely different.

*Crude montan wax* is black or dark brown, but the *purified* product is white or yellowish and of fibrous-crystalline appearance.

The determinations made are usually as follows:

**1. Melting Point.**—As for paraffin wax (*q.v.*, 2).

**2. Acidity.**—The product is dissolved at a gentle heat in a mixture of ethyl and amyl alcohols (1 : 2) and the solution titrated with decinormal potassium hydroxide solution in presence of phenolphthalein (Holde's method).

**3. Saponification Number.**—About 2 grams of the wax are boiled for six hours in a reflux apparatus with 40 c.c. of benzene and 25 c.c. of seminormal potassium hydroxide, the excess of the latter being subsequently titrated with a seminormal acid.

**4. Unsaponifiable Substances.**—2 grams of the wax are saponified as above, the solution evaporated to dryness on a water-bath with 30 grams of granular sand, and the residue extracted in a Soxhlet apparatus with petroleum ether.

Crude montan wax has m.pt. 80–84°, acid number 18–28, saponification number 80–90; the purified product has m.pt. 83–84°, acid number 93–100, and saponification number 94–106.

## LUBRICANTS

Besides heavy mineral oils and vegetable and animal oils and fats (*see* corresponding chapters), use is made as lubricants of mixtures of mineral oils with fatty oils (*see* Heavy Mineral Oils) and of complex mixtures which may contain fats, resins, alkaline and alkaline-earthy soaps, mineral oils, resin and tar oils, in addition to water and mineral matter (lime, talc, graphite, etc.).

Of these complex lubricants the principal ones are the *stiff lubricants*, which include *cart-grease* and usually contain mineral or resin oils with lime soaps and mineral substances, and the *emulsive lubricants*, formed of pale mineral oils with alkaline or ammonium soaps or sulphoricinates.

### 1. Stiff Lubricants

These are solid or semi-solid products of varying appearance. In addition to noting the colour, consistency, homogeneity and odour, the following tests are usually made:

**1. Preliminary Tests.**—These are made to obtain an idea of the composition of the product. The lubricant is first tested to ascertain if it is completely soluble in ether and in petroleum benzine and if it leaves any residue when burnt on platinum foil, absence of such residue excluding the presence of mineral matter and soaps. If it gives with benzene an opalescent solution, which becomes clear on addition of a little absolute alcohol, water is present. The smell emitted when the substance is burnt on platinum foil gives an indication concerning the presence of mineral oils, resins and fats. If ash is left, a little of the lubricant is treated with a mixture in equal proportions of petroleum benzine and absolute alcohol, the liquid being filtered after standing for some hours: the insoluble residue is investigated for lime and other extraneous mineral substances by the ordinary methods.

**2. Melting Point.**—This is determined empirically and approximately as follows: The cylindrical bulb of a thermometer is covered with the substance, without heating, until the shining surface of the mercury is no longer discernible. The thermometer passes through the stopper of a test-tube about 18 mm. in diameter, the tube being immersed in a water-bath which is gradually heated. The temperature at which the substance begins to melt at the surface and that at which a drop of the fused substance falls from the thermometer into the tube are noted.

**3. Water.**—On a boiling water-bath, 3-5 grams of the lubricant are heated in a tared glass dish with 10–15 c.c. of absolute alcohol, the mass being stirred until no further frothing occurs and the liquid becomes clear. When cold, the weight is again taken, the loss representing the moisture.

The latter may also be determined by Marcusson's method (*see* Crude Petroleum).

**4. Acidity.**—As a rule, stiff lubricants contain excess of alkali. When, however, they exhibit acidity, the latter may be determined as follows (Marcusson): 10 grams of the lubricant are heated in a reflux apparatus with 50–100 c.c. of a neutral mixture of 90 parts of benzine and 10 of 96% alcohol, any insoluble residue being filtered off in the hot and washed with the same mixture. The filtrate is mixed with 30 c.c. of 50% alcohol and the acidity measured by titration in the hot with normal caustic soda in presence of phenolphthalein.

**5. Detection and Determination of Soaps.**—From 10 to 12 grams of the lubricant are shaken vigorously and for a long time, in a 250 c.c. separating funnel, with 25 c.c. of dilute hydrochloric acid and 50 c.c. of ether; on standing, two perfectly clear and well-separated layers should be formed. Both layers should be tested with litmus paper to make sure that they are distinctly acid; if not, more hydrochloric acid must be added and the liquid again shaken. The hydrochloric solution is then separated and tested in the ordinary way for bases, especially lime and the alkalies, which occur in the soaps employed in lubricants.

The ethereal layer separated in the preceding operation is washed by shaking with distilled water until neutral, and is then filtered through a *dry filter* into a weighed flask of at least 200 c.c. capacity, the separating

funnel and the filter being washed with ether ; the ether is distilled off on a water-bath, the greater part of it being condensed. If any drops of water remain in the flask, they are eliminated by heating on a boiling water-bath after addition of a few c.c. of alcohol. The flask is again weighed when cold, the increase representing the fatty acids and resins present either free or combined as soaps, plus the neutral fats and non-saponifiable oils ; the percentage of such substance may be denoted by $a$. The acid number is then determined on the whole ethereal extract in the flask itself ; multiplication of the acid number by $\frac{a}{200}$ gives the percentage ($b$) of fatty (or resin) acids found in the free state or as soaps. If from this is subtracted the amount of free acid—calculated with the same coefficient—found as under 4 (above), the remainder represents the acids of the soap ; the amount of soap is then calculated in accordance with the nature of the base it contains.

**6. Detection and Determination of Neutral Animal and Vegetable Oils and Fats.**—The liquid remaining in the flask after the determination of the acidity is heated on the water-bath for about an hour with excess of alcoholic potash and the excess of the latter then titrated ; this gives the saponification number of the neutral fats present. Multiplication of this number by $\frac{a}{200}$ gives the percentage ($c$) of neutral fat.

**7. Investigation of the Unsaponifiable Matter.**—The amount of this may be ascertained from the values already obtained (5 and 6), since it equals $a - (b + c)$.

When, however, it is necessary to separate and examine it, the procedure varies according as resins or resin soaps are present or absent.

In the latter case, about 50 grams of the lubricant are shaken vigorously with at least 200 c.c. of ether in a separating funnel until the oils are dissolved. A kind of emulsion holding the soaps in suspension is thus formed and filtration of this through a large pleated filter gives a clear ethereal solution containing, besides mineral oils, resin oils and tar oils, also any fats present. The ether is distilled off—the last traces being evaporated over a boiling water-bath—and the saponification number determined on a part of the residue. If there is any saponification number, fats are present ; in such case, the non-saponifiable oils are separated by saponification in the cold (*see* Heavy Oils, Chemical Tests, 5), and the mineral, resin and tar oils investigated by the methods indicated for heavy mineral oils.

When, however, resins or resin soaps are present, to separate the non-saponifiable oils, the substance is extracted with acid ether (*see* 5, above), the ether evaporated, the residue washed with 90% alcohol to dissolve the resin, the insoluble residue saponified in the cold (*see* Heavy Oils, Chemical Tests, 5) and the mineral, resin and tar oils investigated as with heavy mineral oils.

When the lubricant contains wool fat, a non-saponifiable residue is obtained which may be confused with mineral oils, but may be distinguished by determining the rotatory power and the iodine number of the residue itself. With mineral oils the specific rotation is usually not more than $[\alpha]_D = 3$ and the iodine number usually below 6 and only rarely above 14. With wool fat, the unsaponi-

fiable residue has the specific rotation + 15° to + 16° or, very occasionally + 10°, and the iodine number is not below 55. Mixtures of mineral oil with the unsaponifiable matter of wool fat give intermediate rotations and iodine numbers. When, however, the unsaponifiable residue contains resin oils, the rotatory power and iodine number no longer give an indication as to the presence of wool fat since these substances also absorb iodine and rotate; in such case, the very high specific gravity of resin oils (0·97–0·99) must be borne in mind.

**8. Detection and Determination of Free Lime and other Mineral Substances.**—About 10 grams of the lubricant are treated for 15 minutes in a reflux apparatus with 50 c.c. of benzine and 5 c.c. of alcohol, the insoluble residue being collected on a filter, washed with the benzine-alcohol mixture, weighed and examined by the ordinary methods to see if it contains lime, calcium carbonate, barium sulphate, talc, graphite and other mineral substances.

***

*Stiff lubricants* vary in composition according to the uses to which they are to be put. Those for stuffing-boxes in steam-engine cylinders are composed of a solid fat (tallow) or of a mixture of tallow with wax and oil. Those for ropes contain solid fats, wax, oil, talc, etc., and those for the chains of cranes, lifts, etc., are similar. Lubricants for rolling mills should melt above 100°; some are composed of pitch from fats or mixtures of this with crude petroleum pitch, while those with a basis of wool fat consist of partially saponified wool fat, with or without resin or acid resin oil. *Briquettes of vaseline*, also used for rolling mills, are formed from mineral oil and soda soap.

Lubricants for gearing are composed of a stiff fat with graphite or talc; oil, tar, resin, wax, paraffin wax and ceresine may also be added.

Lubricants for maintaining the flexibility of belting consist of fish oils mixed with a solid fat (tallow, wool fat, wax). Adhesive lubricants for belting contain, besides these fats, resin, resin oil, wool fat, etc.

Lubricants for the axles of vehicles usually contain tar oil or resin oil in place of mineral oil and mixed lime and resin soaps in place of lime soap and fatty acids.

## 2. Emulsive Lubricants

These are colourless, yellowish or reddish, and often fluorescent liquids, which are mixed with water to form a kind of emulsion; they are sometimes sold ready emulsified and then have the appearance of milky liquids. Besides observing the colour, transparency and odour, and determining the flash point, viscosity and behaviour at low temperatures (*see* Heavy Oils, Physical Tests, 5, 7 and 8), the following tests are made on these oils (*see also* Turkey Red Oil, Chapter XI).

**1. Emulsivity.**—When shaken with water in any proportion, the oil should give a milky emulsion, which should not separate oily drops at its surface even after a long rest. When left overnight at the ordinary temperature, the emulsion of 5 grams of oil with 100 grams of water should undergo no change or should at most deposit yellowish caseous flocks.

**2. Determination of the Water and of the Volatile Solvents.**—The emulsive oils may contain volatile solvents (alcohol, benzine), which are recognised by the smell or, better, by distilling the material on a water-bath and examining the distillate. The amount of volatile solvents and water,

or of water alone when volatile solvent is absent, may be determined as in stiff lubricants (*q.v.*, 3).

**3. Detection and Determination of the Soaps (Fatty Acids and Alkalies).**—A preliminary test is made to ascertain whether ammonia or a fixed alkali is present. Ammonia is detected by the odour and reaction of the vapour emitted when a few grams of the oil are heated in a dish; a fixed residue remaining after calcining indicates the presence of fixed alkali.

(*a*) IN PRESENCE OF AMMONIA. The ammonia is determined by titrating the aqueous emulsion of the oil with N/2-hydrochloric acid in presence of methyl orange. From the amount of ammonia found, the quantity of fatty acids (regarded as oleic acid) combined with it is calculated (1 gram $NH_3$ = 16·542 grams of $C_{18}H_{34}O_2$). The total fatty acids are then determined by boiling the emulsion of the oil with a known quantity, in excess, of N/10–sodium hydroxide solution and titrating the excess of alkali with N/10–acid. The alkali used gives the total fatty acids (calculated as oleic acid) and this quantity, less the combined fatty acids, gives the free fatty acids.

(*b*) IN PRESENCE OF FIXED ALKALI. The free acids are determined by direct titration of the acidity in the usual way, and the total fatty acids by decomposing the soaps with hydrochloric acid, extracting the fatty acids with ether, washing the ethereal layer with water until free from hydrochloric acid, and titrating the acidity of this layer. The combined fatty acids are then given by difference. The aqueous layer is tested qualitatively for alkalies (*see also* Stiff Lubricants, 5).

(*c*) IN PRESENCE OF BOTH AMMONIA AND FIXED ALKALI. The ammonia, the fatty acids combined with it, and the free fatty acids are determined as in (*a*), the total fatty acids as in (*b*) and the fatty acids combined with the fixed alkali by difference.

**4. Detection of Unsaponifiable Substances.**—*See* Stiff Lubricants, 7.

CHAPTER IX

# FATTY SUBSTANCES

Fatty substances consist essentially of combinations of various acids of the fatty series with glycerine, and are obtained from vegetable organisms (especially seeds and fruits) and from various parts of animals. Those liquid at the ordinary temperature are termed *oils*, and those solid, *fats*.

The methods of analysis of fatty substances comprise determinations of certain physical and chemical properties, commonly known as *constants*, although they are constant only within certain limits, and also various other investigations. The first part of the present chapter (*General Methods*) contains descriptions of the more important determinations and tests carried out similarly on all fatty matters. The second part (*Special Part*) deals particularly with the more important fatty substances, the oils, vegetable fats, terrestrial animal fats and fats from fishes and other marine organisms being taken in order. For each class, tables are given showing the more important data relating to the characters of the fatty substances more commonly sold.

Closely analogous to fatty substances are the *waxes*, which consist of compounds of acids with higher alcohols rather than with glycerine , they will be treated after the fats, their general methods of analysis being the same.

The more important industrial products derived from fatty substances, such as stearine, oleine, glycerine, soaps, candles, etc., will be dealt with in the next chapter.

## GENERAL METHODS

### 1. Preparation of the Sample and Preliminary Determination

Before analysis, a fatty substance must be freed from any coarse impurities or water it may contain. For this purpose, a portion of the sample is left for some time in an oven at about 60°, when it clarifies if liquid and melts completely if solid. It is then filtered through one or more filter-papers, care being taken that any water collected under the fat does not fall on to the filter.

With some fats, especially industrial fats, the water, other extraneous matters (mucilaginous substances, residues of vegetable or animal tissues, mineral matter), and total fatty substances have to be determined. The procedure is as follows :

*A*. DETERMINATION OF THE WATER. A flat-bottomed dish containing about 25 grams of coarse siliceous sand, previously ignited, and a glass rod, is dried at 100–105° and weighed. About 10 grams of the sample are then weighed exactly in the dish and mixed well with the sand. The dish is then heated in an oven at 100–105° and weighed at intervals of an hour until two successive weighings are not appreciably different. The loss in weight gives the water; the residue is utilised for determination *C*.

*B*. EXTRANEOUS (NON-FATTY) IMPURITIES. An exact weight (10–20 grams) of the substance is dissolved in a beaker in petroleum ether (b.pt. below 70°) by heating gently on a water-bath. The solution is filtered through a filter dried at 100–105° and tared, the insoluble matter being washed on the filter with petroleum ether until a few drops of the filtrate leave no residue on evaporation. The filter and its contents are then re-dried at 100–105°, and reweighed, the increase giving the *non-fatty* matter.

This may also be deduced by subtracting water + total fat from 100.

*C*. TOTAL FATTY SUBSTANCE. The residue from *A* is placed in a filter-paper cartridge or capsule and extracted with ether or petroleum ether (b.pt. below 70°) in an extraction apparatus. The ethereal solution is collected in a tared dish, evaporated on the water-bath and the residue dried at 100° and weighed.

To obtain the total fatty matter in the case of partially saponified fats (refinery residues and similar products) it is necessary to treat with ether, to shake with dilute sulphuric acid to decompose the soaps, to wash the ethereal liquid with water, to filter and evaporate it, and to dry the residue at 100° and weigh it. In this case the process indicated for turkey red oil (2) may also be followed (*see* next chapter).

If the respective quantities of free and saponified fats are required, the substance is first extracted alone with petroleum ether, the extraction being then repeated in presence of an acid.

## 2. Objective Characters

These characters are of importance in the analysis of fats, since, from the physical condition, colour and odour, at least an approximate idea of the nature of the substance may be obtained. Thus, the smell is sufficient to indicate whether a product is olive oil, tallow, palm oil, wool fat, etc.

## 3. Specific Gravity

This may be determined by means of a Westphal balance or picnometer at 15° with a liquid fat or at a higher temperature with a solid fat. In the latter case, determinations at 100° are especially convenient; the fat is placed in a wide test-tube immersed in a paraffin bath heated at 100°, a densimeter or the float of a Westphal balance being immersed in the fat when the latter reaches a temperature of 98° or 100°.

The Italian official methods prescribe the determination of the specific gravities of oils with the picnometer or with the hydrostatic balance to the fourth decimal figure at 15°. When the measurements are made at higher or lower temperatures, 0·00064 is added or subtracted per degree above or below 15°.

The specific gravity may give an indication of the nature of an oil or fat

and serves especially to distinguish castor oil from other oils or fats from waxes, and may also confirm the purity or otherwise of a fatty oil.

## 4. Melting and Solidifying Points

The most convenient and simple method for determining these constants is as follows: Into a thin-walled glass tube blown to a small bulb *A* at the middle (*see* Fig. 51) sufficient of the fused fat is sucked to fill about one-half of the bulb. When the fat has set, the branch *b* of the tube free from fat is bent into a U-shape in a small flame, and the tube then set aside for as long a time as possible (24 hours if convenient) and, if the fat melts at a low temperature, in a cold place. It is then attached by means of a platinum wire or a rubber ring to a thermometer (Fig. 52) so that the fat occupies the upper part of the bulb, and afterwards suspended in a beaker of water, which is slowly heated. At a certain temperature the fat begins to melt (at this point the heating is discontinued) and flow down the walls of the bulb to collect in the lower part of the bulb. Note is made of the temperature when the fat begins to melt and again when it is all collected in the bottom of the bulb. These temperatures represent the limits between which the fat melts, i.e., its *melting point.*

FIG. 51

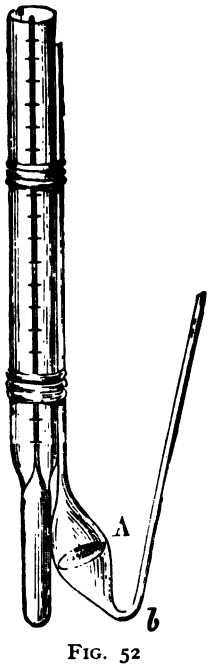


FIG. 52

The fat is then allowed to cool slowly and note made of the temperature when it begins to solidify again and when it is all solid, the *solidifying point* being thus determined.

The solidifying point may be determined more exactly by the method given for the solidifying point of fatty acids (*see* Tallow, 1, Titer Test). A similar method is used for measuring the melting points of fats liquid at the ordinary temperature and of those which become solid at very low temperatures, but in such cases it is necessary to cool externally with water and ice, with ice alone, or with a freezing mixture of snow and salt.

These methods are also used for finding the melting and solidifying points of the free acids obtained from any fat by saponification (*see* 5, below).

The melting and solidifying points, especially those of the fatty acids of fats, serve to characterise many of the latter and to give an indication of their purity (*see* later: the various tables of characters of fats). The solidifying point is also of importance in the determination of the so-called titer of fats (*see* Tallow).

## 5. Saponification

The object of this operation is the scission of fats into their components, i.e., into acids and glycerine (or, with waxes, higher alcohols). It is effected as follows : In a conical flask or a porcelain dish, 20 grams of the fat are heated on the water-bath, with frequent stirring, with 15 c.c. of 50% aqueous caustic potash solution and 30–40 c.c. of 95% alcohol until the liquid becomes homogeneous and clear, this usually occurring after about half an hour.

With substances either containing higher alcohols (wool fat, waxes) or mixed with unsaponifiable substances (mineral oils, various extraneous matters), a clear liquid is not, however, obtained, since the action of the potash causes the separation of the higher alcohols, hydrocarbons and other unsaponifiable substances, which are usually insoluble under the conditions employed. In such a case it is well in order to ensure complete saponification to prolong the heating for an hour or more, with frequent shaking. In some instances, for example, with wool fat or waxes, it is necessary to carry out the reaction under a certain pressure. For this purpose, use is made of a round-bottomed flask, closed with a stopper carrying either a two-bulbed safety funnel charged with mercury or a right-angled tube dipping 5–6 cm. below the surface of mercury in a beaker. In other cases, for special investigations on non-saponifiable substances, *saponification in the cold* is employed ; this is effected by dissolving the substance in ether or petroleum ether, adding a considerable excess of alcoholic caustic potash solution and shaking for a long time.

When the saponification is finished, the product (soap) may be used for various purposes, such as the examination of the unsaponifiable substances or higher alcohols (*see* 19 : Unsaponifiable Substances), the determination of the glycerine (*see* Glycerine), or the separation of the fatty acids.

For the last purpose, the product of the saponification is first freed from alcohol by prolonged heating on a water-bath, the residue being dissolved in hot water, the hot aqueous solution shaken well with excess of dilute sulphuric acid and left at rest on the water-bath until the fatty acids are collected at the surface of the aqueous liquid in a clear layer. The water above the fatty acids is then siphoned off and replaced by fresh hot water, with which the acids are stirred, this washing being repeated three or four times. Instead of siphoning off the water, the latter and the fatty acids may be decanted on to a moist filter and the acids washed with hot water on the filter itself until the filtrate ceases to give the reaction for sulphuric acid. The washed fatty acids, in a flat dish, are kept for some time (about an hour) in a steam-oven and then filtered through a dry filter. They are then ready for various determinations, such as the melting and solidifying points, acid number, iodine number, solid and liquid acids.

## 6. Behaviour towards Solvents

The ordinary solvents for fatty matters are ether, benzene, carbon disulphide and tetrachloride, chloroform and petroleum ether. All fats dissolve in these liquids (castor oil, however, is almost insoluble in petroleum ether). In alcohol fatty substances are more or less soluble according to

their nature and the circumstances, and the same holds with glacial acetic acid.

The test of solubility in the ordinary solvents, e.g., in ether, serves to show if a fatty substance is pure or mixed with extraneous substances insoluble in that solvent. The test of solubility in alcohol may be used to distinguish castor oil and fatty acids in general (easily soluble even in the cold) from the majority of other oils and fats, which are mostly very slightly soluble, especially in the cold.

## 7. Acid Number

## (Acidity Index)

The acid number is defined as the number of milligrams of potassium hydroxide (KOH) necessary to neutralise the free fatty acids in a gram of the fatty substance. From this number the amount of free acids contained in a fat may hence be deduced. The determination is made as follows:

An exact weight of about 5 grams of the fat is heated in a flat-bottomed flask on a water-bath with 50–60 c.c. of 96% alcohol,[1] and kept well shaken until the alcohol begins to boil. Seven or eight drops of phenolphthalein solution (1% in 95% alcohol) are then added and the liquid titrated with decinormal potassium hydroxide solution until a persistent red colour appears. If solid fat separates during the titration, the flask is placed on the water-bath until the fat melts. The volume of potash solution used gives the acid number (1 c.c. N/10-KOH = 0·00561 gram KOH).

From the acid number thus obtained the percentage of free acids in a fat may be calculated; this is usually expressed as oleic acid, the molecular weight of which is 282 (corresponding with 56·1 of KOH). The calculation is made by the formula,

$$x = \frac{n \times 0{\cdot}0282}{p} \times 100,$$

where $n$ is the number of c.c. of N/10-KOH used, $p$ the weight of the substance and $x$ the percentage of oleic acid in the substance.

The free acids in a fat are sometimes expressed as sulphuric anhydride ($SO_3$), the formula then becoming

$$x = \frac{n \times 0{\cdot}004}{p} \times 100,$$

$x$ in this case being the percentage of $SO_3$.

EXAMPLE: For 5·223 grams of fat, 4·2 c.c. of N/10-KOH were used. Since 1 c.c. of the potash corresponds with 0·00561 gram of KOH, i.e., with 5·61 milligrams, the acid number will be

$$\frac{5{\cdot}61 \times 4{\cdot}2}{5{\cdot}223} = 4{\cdot}51.$$

[1] The alcohol should first be rendered neutral to phenolphthalein by means of decinormal caustic potash. If the fat is only slightly soluble in alcohol or, more especially, if it gives a highly coloured solution in alcohol, 100–150 c.c. of the latter must be taken or a smaller quantity of substance: e.g., 2 grams are treated with 50–100 c.c. of the alcohol. In place of alcohol alone, a mixture of (1) 1 vol. of alcohol and 4 vols. of ether, or (2) 1 vol. of absolute alcohol and 2 vols. of amyl alcohol may be used as solvent, without heating.

Further,

$$\text{Percentage of oleic acid} = \frac{4{\cdot}2 \times 0{\cdot}0282}{5{\cdot}223} \times 100 = 2{\cdot}267.$$

$$\text{Percentage of } SO_3 = \frac{4{\cdot}2 \times 0{\cdot}004}{5{\cdot}223} \times 100 = 0{\cdot}321.$$

The acidity of a fat may also be expressed in *degrees*, which are distinguished as *Köttstorfer* and *Burnstyn* degrees. The former represent the number of c.c. of normal KOH solution necessary to neutralise the free acidity of 100 grams of a fat.

Burnstyn degrees (formerly used, especially to express the acidity of lubricating oils) represent the number of c.c. of normal KOH required to neutralise the acidity of 100 c.c. of oil, the test being carried out as follows: 100 c.c. of the oil are shaken with 100 c.c. of 90% alcohol; when the latter has separated and become clear, 25 c.c. of it are titrated with normal KOH, tincture of turmeric or phenolphthalein being used as indicator. The number of c.c. used, multiplied by 4, gives the Burnstyn acidity of the oil.[1]

Interconversion of the acidities expressed in different ways may be effected by means of the following table:

| Acid Number (mgrms. KOH per gram of substance). | Oleic Acid. % | Sulphuric Anhydride. % | Köttstorfer Degrees (c.c. N-KOH per 100 grams of substance). |
|---|---|---|---|
| 1 | 0·5027 | 0·0713 | 1·782 |
| 1·9893 | 1 | 0·1418 | 3·546 |
| 14·0250 | 7·0500 | 1 | 25·000 |
| 0·5610 | 0·2820 | 0·0400 | 1 |

The acid number of fatty substances is very variable. As a rule, fresh or recently-prepared fats contain little or no free acid. With keeping, especially if not well protected against the simultaneous action of air and light, the acidity increases, slowly at first and more rapidly later. The acid number is of importance in judging edible oils and lubricants, neither of which should contain more than certain limiting proportions of free acid.

## 8. Saponification Number

By saponification number is meant the number of milligrams of potassium hydroxide (KOH) necessary to saponify completely 1 gram of a fatty substance. From this number the quantity of total acids, either free or combined, in a fat may be deduced. The determination is made as follows.

REAGENTS required are:

(1) *Alcoholic caustic potash solution* (about seminormal). Prepared by dissolving about 32 grams of pure caustic potash in a little water and making up to 1 litre with 95% alcohol free from fusel oil.[2] The solution

[1] The acidity of an oil determined in this way is always decidedly lower than that determined by the preceding methods.

[2] When ordinary alcohol is used, the solution soon turns brown. Suitable alcohol is obtained from good, commercial 95% alcohol by adding, and shaking with, powdered potassium permanganate until a persistent red coloration is formed. The liquid is left for some hours and distilled, in an apparatus provided with a dephlegmator, with

is kept in a bottle closed with a rubber stopper through which passes a 25 c.c. pipette.

(2) *Seminormal hydrochloric acid.*

(3) *Alcoholic phenolphthalein solution* (1% in 95% alcohol).

PROCEDURE. In a conical 150–200 c.c. flask, 1–2 grams of the fat are weighed and treated with 25 c.c. of the alcoholic potash solution, the pipette being emptied always in the same way. The flask is closed with a stopper through which passes a glass tube about a metre long to serve as a reflux condenser and heated on a boiling water-bath, with occasional shaking, for half an hour or rather more (*see* Saponification, 5).

The flask is then removed from the bath and the excess of potash remaining free titrated with seminormal hydrochloric acid in presence of 8–10 drops of the phenolphthalein solution.[1]

A *check* experiment with 25 c.c. of the caustic potash solution alone (without fat) is made at the same time and under the same conditions as the actual test.[2]

From the difference between the volumes of seminormal hydrochloric acid used in the check experiment and in the actual test with the fat, the amount of potash (milligrams) necessary for the complete saponification of 1 gram of the fat is calculated.

EXAMPLE: 1·524 gram of a fat, saponified with 25 c.c. of alcoholic potash, required 11·9 c.c. of seminormal hydrochloric acid to neutralise the excess of potash. In the check experiment, 22·5 c.c. of the acid were required for 25 c.c. of alcoholic potash. Since 1 c.c. N/2-HCl = 0·02805 gram of KOH, the amount of KOH necessary to saponify 1·524 gram of fat is (22·5–11·9) 0·02805 gram = 0·2973 gram, so that the amount for 1 gram of fat is 0·195 gram. The saponification number of the fat is hence 195.

The saponification number is of importance for distinguishing between different fats and waxes and especially for the analysis of mixtures of fatty substances with non-saponifiable matter (mineral oils, resin oils, etc.).

The majority of fatty substances have a saponification number between 190 and 200, but the oils of the Cruciferæ (colza oil, ravison oil, etc.), castor oil, grapeseed oil, and a few other oils, have values below 190.

Coconut oil, palm-kernel oil, certain other vegetable fats, and butter have numbers above 200. Waxes have very low saponification numbers (below 100).

## 9. Ester Number

The ester number denotes the number of milligrams of caustic potash necessary to saponify the neutral fat (neutral esters) in one gram of a fatty substance. With fats which do not contain free acids, the ester number is equal to the saponification number; when, however, free acids are present,

a little powdered calcium carbonate at such a rate that 50 c.c. pass over in 20 minutes. To test the distilled alcohol, 10 c.c. are boiled with 1 c.c. of 50% caustic potash solution and the liquid allowed to stand for 20 minutes to see if any colour develops. If so, the alcohol is unsuitable for preparing alcoholic potash and should be again treated with permanganate.

[1] When the fat gives a highly coloured solution with the alcoholic potash, it is advisable to dilute the liquid considerably with neutral alcohol before titrating, in order that the neutral point may be determined with accuracy.

[2] Two blank experiments and two actual tests should always be made and the mean of the results taken, provided t hat these do not differ greatly.

the ester number is given by the difference between the acid and saponification numbers.

The ester number has importance especially for the analysis of beeswax.

## 10. Volatile Acid Number (Reichert-Meissl Number)

By this is meant the number of c.c. of decinormal alkali necessary to neutralise the volatile acids, soluble in water, obtained from 5 grams of a fatty substance under definite conditions.

Reichert's original method has been modified in various ways, the modification proposed by Leffmann and Beam and by Polenske being now preferred.

In a flat-bottomed, 300 c.c. flask of resistant glass (*A*), exactly 5 grams of the fatty substance (filtered oil or molten fat) are heated over a small flame with 20 grams of pure glycerine and 2 c.c. of caustic soda solution (100 grams of pure sodium hydroxide in 100 grams of water) until the liquid froths and becomes clear and homogeneous (5–8 minutes). The liquid soap thus obtained is allowed to cool to 80–90° and is then shaken with 90 c.c. of distilled water at the same temperature, and heated if necessary, until solution is complete. 50 c.c. of dilute sulphuric acid (25 c.c. of the pure conc. acid to the litre) and 0·6–0·7 gram of roughly powdered pumice are then added and the liquid distilled into a 110 c.c. flask.

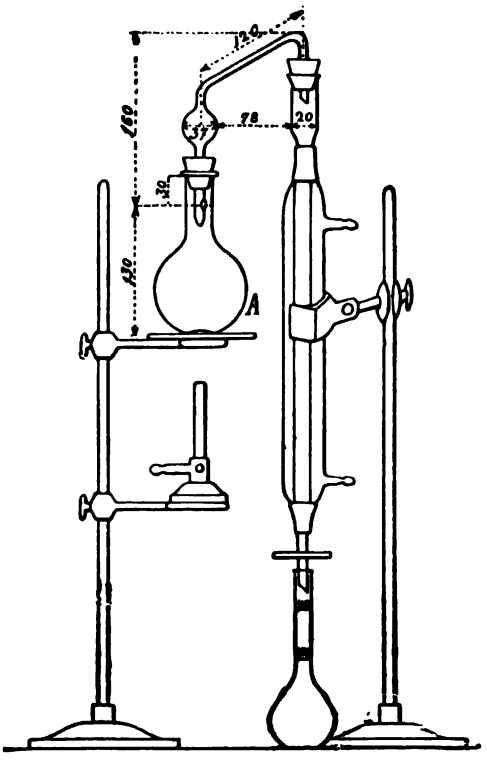


FIG. 53

For this distillation the condenser and accessory apparatus have the form and dimensions (m.m.) shown in Fig. 53. The distilling flask is supported on an asbestos card on a ring 6·5 cm. in diameter, and the flame should be such that the 110 c.c. of distillate are collected in about 19–21 minutes.

When the 110 c.c. of distillate are collected, the flame is extinguished and the collecting flask replaced by another vessel and left in water at 15° without shaking for 10 minutes. It is then stoppered, inverted four or five times to mix the liquid but not to shake it too much, and filtered through a dry filter 8 cm. in diameter, 100 c.c. of the filtrate being titrated with decinormal potassium hydroxide solution in presence of 3–4 drops of 1%

alcoholic phenolphthalein solution. The number of c.c. of N/10-alkali required, increased by one-tenth, represents the volatile acid number.

For each series of determinations a blank experiment must be made with the same glycerine (20 grams), sodium hydroxide solution (2 c.c.) and sulphuric acid (50 c.c.) and under the same conditions as in the actual test. The number of c.c. of N/10-alkali used in this blank experiment is subtracted from the volume used in the actual test.

The determination of the volatile acid number may be carried out along with that of the Polenske number (*see* Butter, 15, in Chapter II of Vol. II).

The Italian official method for determining the volatile acid number is, for oils, Wollny's modification of the Reichert-Meissl method, and for butter, Leffmann and Beam's modification, which differs from that described above in using a glycerine and soda solution previously prepared (125 c.c. of glycerine and 25 c.c. of 5% sodium hydroxide solution heated until the water is eliminated) in place of glycerine and soda separately, and in a few other details.

The volatile acid number is of importance in the analysis of only a limited number of fats, principally butter. With most oils and fats, the number is less than 1 ; coconut oil, palm-kernel oil, croton oil, cacao butter and a few other fats have numbers above 1 (up to 14), while for butter the value is 28. Some fish oils and other marine animal oils (dolphin, whale) have variable and sometimes moderately high volatile acid numbers.

## 11. Acetyl Number

This represents the number of milligrams of potassium hydroxide corresponding with the quantity of acetyl ($C_2H_3O$) combining with 1 gram of fat or wax, or, more usually, with 1 gram of fatty acids or higher alcohols (unsaponifiable substances) obtained from a fat or wax.

This number is determined as follows : About 20 grams of the substance or of the free fatty acids obtained in the manner described under " Saponification " (*see* 5, above) or of unsaponifiable substances (high alcohols, etc.) obtained as indicated under " Non-saponifiable Substances " (*see* 19, below) are boiled for 2 hours with an equal volume of acetic anhydride in a flask fitted with a reflux condenser, the mixture being subsequently transferred to a beaker, mixed with 500 c.c. of hot water and boiled for half an hour. The supernatant water is then siphoned off and the residue again washed in the same way, this treatment being continued until the water no longer becomes acid ; this usually requires four or five washings. The acetylated product is then filtered through a dry paper in an oven at 100° and used for the determination of the acidity number—known as the *acetyl acid value* —and the saponification number—the *acetyl saponification number*. The acetyl number is given by the difference between these two.

For these determinations, 3-5 grams of the acetylated product are dissolved in 50 c.c. of 90% alcohol and the solution titrated with seminormal potassium hydroxide solution in presence of phenolphthalein ; this gives the acetyl acid number. The same liquid is then boiled for a short time in a water-bath with excess of N/2-KOH and alcohol and the excess of alkali titrated with N/2-HCl, this giving the acetyl saponification number.

EXAMPLE : 3·402 grams of acetylated fatty acids from castor oil required

for neutralisation 17·3 c.c. of N/2-KOH, i.e., 17·3 × 0·02805 = 0·4852 gram KOH, the acetyl acid value being therefore

$$\frac{485{\cdot}2}{3{\cdot}402} = 142{\cdot}6.$$

After addition of a further quantity of 30 c.c. of N/2-KOH and boiling, 11·5 c.c. of N/2-HCl were necessary to neutralise the excess of potash. The potash consumed in the saponification of the acetyl compounds was hence 30–11·5 = 18·5 c.c., corresponding with 18·5 × 0·02805 = 0·5189 gram KOH; for 1 gram of acetylated acids the amount of KOH will be

$$\frac{518{\cdot}9}{3{\cdot}402} = 152{\cdot}5.$$

The acetyl number is therefore 152·5, and the acetyl saponification number, 142·6 + 152·5 = 295·1.

The acetyl number is related to the quantities of hydroxylated acids and higher alcohols in the fatty substances, these being especially large in castor oil, grapeseed oil, waxes and blown or oxidised oils. It is consequently of some importance for the identification of these fats and for the analysis of waxes.

## 12. Iodine Number

This expresses the number of grams of iodine 100 grams of a fatty substance are capable of fixing under definite conditions. It may be determined in the two following ways:

*A*. **Hübl's Method.**—REAGENTS required:—

1. *Iodine solution.* 25 grams of iodine are dissolved in 500 c.c. of 95% alcohol (puriss.); in another 500 c.c. of the same alcohol, 30 grams of mercuric chloride are dissolved and the solution filtered, if necessary. The two solutions are stored separately in tightly stoppered bottles in a cold dark place, equal volumes of them being mixed in the quantities required for the number of tests to be made, about 48 hours before use.

2. *Potassium iodide solution.* 10 grams of potassium iodide (puriss.) quite free from iodate are dissolved in 100 c.c. of water.

3. *Starch solution.* 1 gram of starch is made into a paste with a little cold water and then poured into about 300 c.c. of boiling water, stirred and left to settle; when cold, the clear supernatant liquid is poured off for use as indicator. *Soluble starch* also may be employed, this being prepared by digesting potato starch with dilute hydrochloric acid (D 1·05) for a week, then washing with water by decantation until the washing water is free from hydrochloric acid and drying between filter-papers at a moderate temperature; 1 gram of this starch is dissolved in 100 c.c. of hot water.

4. *Sodium thiosulphate solution.* 25 grams of crystallised sodium thiosulphate (puriss.) are dissolved in distilled water to 1 litre, and the strength of the solution determined by Volhard's method, as follows: 20 c.c. of a solution containing 3·863 grams of pure potassium dichromate per litre are shaken with 10 c.c. of the aqueous 10% potassium iodide solution and 5 c.c. of hydrochloric acid (D 1·10); 100–150 c.c. of water are then added and the liberated iodine titrated with the sodium thiosulphate solution, a little of the starch paste being added towards the end of the titration. Since 20 c.c. of the above potassium dichromate solution set free 0·2 gram of iodine from potassium iodide in presence of hydrochloric

acid, the number of c.c. of thiosulphate used corresponds with 0·2 gram of iodine.

5. *Chloroform*, which should be pure.

PROCEDURE. In a thin glass bulb the fatty substance (as it is, if liquid, or fused if a solid, but always previously dehydrated and filtered: *see* 1: Preparation of the Sample) is weighed, 0·1–0·2 gram being taken of a drying oil, 0·2–0·3 gram of a semi-drying oil, 0·3–0·4 gram of a non-drying oil or 0·4–0·8 gram of a solid fat. The bulb is placed in a half-litre glass bottle with a tight ground stopper, the bottle being held obliquely and suddenly shaken so as to break the bulb against the walls. The fat is then dissolved in 15 c.c. of chloroform and treated with 25 c.c. of the mixture in equal volumes of the iodine and mercuric chloride solutions (prepared about 48 hours earlier), care being taken in all cases to empty the pipette in the same way so that exactly the same volume of solution is used. The liquid is carefully shaken and the bottle stoppered and kept in a dark cool place (15–18°) for 4–6 hours with non-drying or semi-drying oils or for 18-24 hours with drying oils. At the end of this time, 15-20 c.c. of the potassium iodide solution are introduced, the stopper, neck and walls of the bottle being washed with this solution and with about 200 c.c. of distilled water subsequently added. The excess of iodine is then titrated with the thiosulphate solution, which is slowly run in until the aqueous liquid and the chloroform beneath appear only pale yellow; about 5 c.c. of the starch solution are then added and the titration completed.

This test is always made in duplicate and at the same time two *blank* experiments are carried out with the same proportions of solutions and under the same conditions, but without the fatty substance. The amounts of iodine in the two checks are titrated one before and the other after the actual test, the mean value being taken.

This mean is deducted from the mean value obtained in the tests with the fat, the remainder representing the amount of iodine absorbed by the fat, and this, calculated as percentage, is the iodine number.

*B.* **Wijs's Method.**—In this method, the alcoholic solution of iodine and mercuric chloride is replaced by an *acetic acid solution of iodine monochloride* prepared as follows:

8 grams of pure iodine trichloride and 8·5 grams of iodine are dissolved separately in pure glacial acetic acid (99%) on a water-bath and in dry, closed vessels to avoid absorption of moisture. When cool, the two solutions are transferred to the same 1-litre flask and made up to volume with pure glacial acetic acid.

It is necessary to ascertain that the acetic acid is at least 99% and that it is pure: when heated with potassium dichromate and conc. sulphuric acid it should give no coloration even after some time.

Further, to dissolve the fatty substance use is made of pure *carbon tetrachloride* (also to be tested with dichromate and sulphuric acid, as with the acetic acid).

The solutions 4, 2 and 3 (sodium thiosulphate, potassium iodide and starch) of Hübl's method are used also in this case.

The procedure is the same as with Hübl's method, excepting that the

time of contact of the fatty substance with the iodine solution is reduced to about an hour for non-drying or but slightly drying oils and fats and to about two hours for the others. The calculation is made as with Hübl's method.

EXAMPLE: For 0·352 gram of olive oil 24·90 c.c. of thiosulphate were required, and in the check experiment, 48·80 c.c. The quantity necessary to decolorise the excess of iodine is, therefore, 48·8 — 24·9 = 23·90 c.c.

Assuming that 0·2 gram of iodine corresponds with 16·5 c.c. of thiosulphate, i.e., 0·01212 gram with 1 c.c., the amount of iodine absorbed by 0·352 gram of the oil is 23·9 × 0·01212 = 0·2896 gram, so that the iodine number is

$$\frac{0{\cdot}2896 \times 100}{0{\cdot}325} = 82{\cdot}27.$$

As a rule the iodine numbers obtained by the second method (Wijs's) are rather higher than those given by Hübl's method.

The determination of the iodine number is of great importance for the analysis of fatty substances, since it serves to characterise many of them and to indicate if they are pure or mixed. Drying oils (linseed, hempseed, walnut, poppy-seed, madia, Japan wood, etc.) and fish oils (sardine, anchovy, herring, cod) have very high iodine numbers, which usually exceed 120. The non-drying oils (olive, arachis, almond) have iodine numbers below 100. The semi-drying oils (colza, cottonseed, sesamé, maize) have intermediate values. Iodine numbers between 30 and 60 are usually shown by vegetable fats, excepting coconut oil, palm-kernel oil and certain so-called vegetable waxes (myrtle, Japan), which have values below 11. With the animal fats the iodine number is not very high, being usually less than 90.

With each individual fat the iodine number may vary between fairly wide limits, in accordance with the method of preparing the fat, with the degree of maturity of the fruit or seed yielding it, with the conditions of storing and age of the fat, etc. Very wide variations are, however, exceptional, and in most cases the iodine number keeps moderately constant (*see*, for example, Olive Oil), so that it may be used for the approximate determination of the respective quantities of fats in a mixture of two of known character—the calculation being made according to the law of mixtures.

The causes of pronounced variations in the iodine number are various, but of especial importance are the age and storage conditions of the fat. In general, old and badly stored (rancid) fats have iodine numbers lower than those of the corresponding fresh and well-kept fats; this is notably the case with drying oils, which readily absorb atmospheric oxygen.

## 13. Absolute or "Inner" Iodine Number

This represents the weight of iodine absorbable by 100 parts of the liquid fatty acids obtainable from a fatty substance.[1] It is determined on the liquid fatty acids isolated by Tortelli and Ruggeri's process (*see* later: 18).

Ten or fifteen drops of the liquid acids, just prepared, are weighed in a bulb of thin glass and the iodine number then determined as indicated in the preceding article (12).

[1] It is the liquid portion of the fatty acids, separated as described later, that contains the unsaturated fatty acids (oleic, linoleic, linolenic, etc.), which have the property of fixing iodine, so that the iodine number of this portion is properly called the absolute iodine number.

The absolute iodine number follows the same course as the relative one, being very high in the drying oils (over 150) and the semi-drying oils (120–155) and lower in the non-drying oils (about 100). For animal fats the number is usually 90–100, but in rare cases slightly exceeds 100 (in some American lards). This number is of especial importance in the analysis of lard and its substitutes (*see* Lard).

## 14. Insoluble, Fixed Fatty Acid Number (Hehner Number)

This number represents the quantity of non-volatile fatty acids insoluble in water contained in 100 grams of a fatty substance. Its determination is carried out as follows:

5 grams of the fat, weighed into a conical flask, are treated with 50 c.c. of 90% alcohol and 5 c.c. of 50% caustic potash solution. The flask is closed with a stopper through which passes a long glass tube to serve as reflux condenser and is then heated on a water-bath with frequent shaking until saponification is complete. The stopper and tube are then removed and the alcohol distilled off, the last traces being expelled from the open flask in a boiling water-bath. The soap is dissolved in 150 c.c. of hot water and then decomposed with a slight excess of dilute sulphuric acid. The flask is then left on the water-bath until the fatty acids have collected in a homogeneous layer at the surface, after which it is allowed to cool somewhat and kept in cold water (at 10–15°) for about an hour, so that the fatty acids set to a solid mass. The aqueous liquid is then filtered through a smooth, thick paper filter, previously dried at 100° and weighed in a weighing bottle. A further quantity of 200 c.c. of hot water is added to the flask, which is shaken, left on the water-bath for 15 minutes, allowed to cool somewhat and placed in cold water, the aqueous liquid being filtered as before. This treatment is repeated five or six times until the filtrate no longer reddens a litmus paper immersed in it for 10 minutes. The fatty acids are then completely melted by addition of a little boiling water and the whole transferred to the filter, the flask being freed from the last traces of the fatty acids by several small quantities of hot water, and care taken that a few drops of water always remain under the acids on the filter. When all the acids are on the filter, all the water on the latter is allowed to flow away and the filter immediately placed carefully in the weighing bottle, which is dried at 100° and weighed at the end of each half-hour until the difference between two successive weighings is less than 1 milligram. The weight of the fatty acids thus obtained, calculated for 100 grams of substance, gives the insoluble fixed acid number sought.[1]

The insoluble fatty acid number varies little for most oils and fats, being usually 95–96·5 for oils and 94·5–97 for fats. Some vegetable and animal oils and fats are, however, exceptional, especially if they are rich in volatile or

[1] With highly altered fats, which may contain appreciable proportions of hydroxy-acids, or with fats which may be mixed with gummy or gelatinous substances, etc. (such as sanse oils or bone oils), it is well to treat the insoluble fatty acids with cold carbon disulphide or petroleum ether to remove hydroxy-acids and other extraneous substances (Gianoli: *Ann. Soc. chim. de Milano*, 1902, p. 155).

soluble fatty acids. Thus the following oils : Crotan Elliotianus, curcas, grape-seed, Macassar, palm-kernel, cacao, coconut, dogfish, dolphin (from the head), have values varying from 87 to 94 ; dolphin oil (from the jaw), spermaceti and wool fat, from 59 to 66. The number for butter is 86-90, and those for the waxes are also comparatively low.

## 15. Hydroxy-acids

The determination of the quantity of hydroxy-acids contained in a fatty substance is effected by Fahrion's method, based on the insolubility of the hydroxy-acids and the solubility of all the fatty acids, in light petroleum.

From 3 to 5 grams of the fatty substance are saponified in the usual way (*see* 5 : Saponification), the alcohol evaporated, the soap dissolved in 50–70 c.c. of hot water, decomposed in a separating funnel with dilute hydrochloric acid, shaken well with 100 c.c. of petroleum ether (boiling below 80°) and left until the two separate layers are perfectly clear. The aqueous layer is run off and then the petroleum ether, the insoluble hydroxy-acids, which remain adherent to the walls of the funnel, being washed several times with petroleum ether and afterwards dissolved in boiling alcohol. The alcoholic solution is evaporated to dryness in a tared dish and the residue dried at 100° and weighed.

This method allows of the determination of the hydroxy-acids produced by the oxidation, either natural or artificial, of an oil or fat. Such a determination has special importance in the analysis of boiled linseed oil and of the so-called blown oils, which are rich in hydroxy-acids.

## 16. Lactones or Internal Anhydrides

The simplest method of determining the content in internal anhydrides of a mixture of fatty acids is based on the following principle : in a mixture of pure insoluble fatty acids it is found that the acid number is equal to the saponification number, so that there is no ester number. If, however, the fatty acids are accompanied by lactonic anhydrides, the saponification number differs from the acid number. This is because the fatty acids are saturated immediately in the cold by potash, whilst the lactones must be boiled with excess of alcoholic potash in order to be neutralised.

Hence, to ascertain the content in lactones of a mixture of fatty acids, it is sufficient to determine by the ordinary methods the acid number and the saponification number and, consequently, the ester number. From the latter the content of lactone may be calculated, when the molecular weight from which the ester number is calculated is known (usually the lactone content is calculated as stearolactone).

In order that the acid, saponification and ester numbers of the fatty acids may not be confused with the respective numbers for the fatty substances, it has been proposed to call the former : *Constant acid number, constant saponification number* and *constant ester number.*

EXAMPLE : If a mixture of fatty acids gives the constant acid number 160 and the constant saponification number 195, the constant ester number will be 35.

The ester number of stearolactone being 198·9, the mixture examined contains

$$\frac{100 \times 35}{198{\cdot}9} = 17{\cdot}66\%$$

of stearolactone.

The determination of the lactones is of some importance with certain industrial products of fatty matters, e.g., turkey red oil and distilled stearine, the latter especially being rich in stearolactone, i.e., in the internal anhydride of hydroxystearic acid.

## 17. Determination of the Glycerine

The simplest method of determining if glycerine is present in a substance is to heat a little of the latter to boiling with a few crystals of potassium bisulphate : in presence of glycerine, unpleasant, irritating odours of acrolein are evolved, while a strip of filter-paper soaked in concentrated sodium nitroprusside solution containing a little piperidine is dyed an intense blue if placed in the mouth of the test-tube.

The glycerine in fatty substances may be determined *indirectly*, knowing that in the saponification of neutral fats 1 mol. of glycerine (92 grams) corresponds with 3 mols. of potassium hydroxide (168·3 grams). Multiplication of the ester number (*see* 9, above) by 0·05466 also gives the glycerine content. This method is, however, only applicable when the fat does not contain higher alcohols, unsaponifiable substances, etc.

To determine the glycerine *directly*, the fatty substance (20 grams) is saponified in the ordinary manner (*see* 5 : Saponification), the soap decomposed by an acid, the fatty acids separated by filtration, and the glycerine in the aqueous filtrate determined by one of the methods given in the next chapter for the quantitative analysis of glycerine.

## 18. Determination of the Solid and Liquid Fatty Acids

The fixed (or insoluble) fatty acids entering into the composition of fatty substances may be divided into two principal groups : solid, saturated acids belonging to the acetic acid series and represented especially by stearic and palmitic acids (sometimes also by arachic and lignoceric acids), and liquid, unsaturated fatty acids belonging to the acrylic series and to other less hydrogenated series and represented especially by oleic acid and often also by linoleic, linolenic and ricinoleic acids.

The best method for separating these two groups of acids is based on the insolubility of the lead salts of the solid acids, and the ready solubility of those of the liquid acids, in ether. Special methods serve for the separation of the individual solid acids and the individual liquid acids.

**1. Separation and Determination of the Solid and Liquid Acids.**— For such separation Tortelli and Ruggeri's method is used :

20 grams of the fat are saponified in the usual way (*see* Saponification), the soap being dissolved in water and the solution neutralised towards phenolphthalein with acetic acid. Meanwhile, 300 c.c. of 7% neutral lead acetate solution are heated in a conical flask and when this liquid reaches the boil the soap solution is run into it in a thin stream, the lead solution being kept stirred. The flask is then immersed in cold water

for about 10 minutes with continual shaking, the lead soap becoming attached to the sides and bottom of the flask, while the liquid becomes clear. The whole of the liquid is then decanted off and the soap washed with three successive quantities of 200 c.c. of hot water (70–80°). The water is drained off, the beaker cooled, the last drops of water adhering to the soap removed by means of filter-paper, and 220 c.c. of ether added. The flask is well shaken and then fitted with a reflux apparatus and the liquid gently boiled on a water-bath for 20 minutes with occasional shaking and subsequently immersed in cold water (4–5°) for two hours. The clear ether is filtered into a separating funnel,[1] care being taken to let as little as possible of the undissolved soap fall into the filter. The residue in the flask is then heated for 20 minutes with a fresh quantity of 100 c.c. of ether under a reflux condenser and the flask afterwards stoppered and placed on one side immersed in cold water.

Meanwhile the filter is washed with a little very cold ether which is caught in the separating funnel containing the other filtrate. The well-covered *filter is placed on one side*, while the ethereal liquid in the separating funnel is vigorously shaken with 150 c.c. of 20% hydrochloric acid to decompose the lead soap of the liquid acids and then left to stand until the ether has collected at the surface in a clear layer. The lower aqueous layer, together with the precipitated lead chloride, is run off, the treatment repeated with 100 c.c. of hydrochloric acid, and the ethereal solution then washed three times with distilled water (150 c.c. each time). Finally, the bulk of the ether is distilled off and the last traces driven off on a water-bath while a current of carbon dioxide is passed.

The liquid acids thus obtained are weighed and calculated to 100 parts of the substance. These liquid acids, provided they are kept out of contact with the air, may be further utilised for the detection of cottonseed oil and sesamé oil (*q.v.*) and for the determination of the absolute iodine number (*see* 13, above).

The lead soap of the solid fatty acids, left undissolved in the flask immersed in cold water, is collected on the filter placed on one side, as mentioned above, and washed well with very cold ether and then introduced into a separating funnel where it is shaken with ether and hydrochloric acid as in the case of the liquid acids.

The ethereal solution of the solid fatty acids is distilled and the residue dried in an oven at 100° and weighed. For greater accuracy, the weight found may be increased by the quantity of solid acids (stearic and palmitic) corresponding with their lead soap remaining dissolved in the ether, knowing that 50 c.c. of anhydrous ether at the ordinary temperature dissolve 0·0074 gram of lead stearate and 0·0092 gram of lead palmitate; these amounts correspond with 0·0054 gram of stearic and 0·0065 gram of palmitic acid. The solid acids thus separated may then be utilised for other investigations, e.g., for that of the arachidic and lignoceric acids (*see* Arachis Oil).

Other gravimetric methods for the quantitative separation of the solid from the liquid fatty acids are (1) those of *David*[2] and *Falciola*,[3] based on

[1] For very exact determinations the funnel should be cooled externally with ice.
[2] *Ann. de chim. analyt.*, 1911, p. 8. [3] *Gazz. chim. ital.*, 1910, II, pp. 217 and 425.

the fact that the ammonium salts of the solid acids are insoluble, and those of the liquid acids soluble, in alcohol, and (2) that of *Fachini and Dorta*,[1] based on the insolubility of the solid fatty acids and their alkali salts in cold acetone; this solvent also serves to separate stearic and palmitic acids from myristic and lauric acids.

The content of liquid and solid acids in a fatty substance may also be deduced from the absolute and relative iodine numbers. If $I_r$ is the relative iodine number or that of the fat as such, and $I_a$ the absolute iodine number or that of the liquid fatty acids extracted from the fat, 1 part by weight of iodine corresponds with $\frac{100}{I_a}$ parts by weight of liquid acids (since $I_a$ corresponds with 100 parts by weight of liquid acids). With the quantity of iodine $I_r$ absorbed by 100 parts of the fat there correspond $\frac{100I_r}{I_a}$ parts of liquid fatty acids, this last fraction giving the percentage of liquid fatty acids in the fatty substance.

When a mixture of palmitic, stearic and oleic acids along is dealt with, the content of oleic acid may be calculated from the relative iodine number of the mixture, since it is known that the theoretical iodine number of oleic acid is 90·07. Thus, if $I$ is the relative iodine number of the mixture and $O$ the percentage of oleic acid sought,

$$O = \frac{100 \times I}{90{\cdot}07} \text{ or } O = 1{\cdot}1102I.$$

Lastly, it must be pointed out that, with mixtures of the three acids named above, the content of liquid and solid acids may be determined by means of the solidification point of the mixture, use being made of Dalican's table (*see* Tallow and Stearine, 1).

**2. Determination of the Stearic Acid.**—The content of stearic acid in a mixture of fatty acids obtained by saponification of a fat may be determined by Hehner and Mitchell's method, which is based on the fact that stearic acid is very slightly soluble in alcohol at 0°, whilst palmitic acid is much more soluble and the liquid acids readily soluble.

From 0·5 to 1 gram of the fatty acids, if solid, or 5 grams if liquid, are dissolved in 100 c.c. of alcohol of D = 0·8183 (94·4% alcohol) already saturated at 0° with pure stearic acid; the solution is then cooled to 0° and filtered and the residue washed with alcohol saturated with stearic acid, working always at 0°; finally the stearic acid remaining insoluble is weighed.

This method is applicable especially to mixtures of stearic acid with palmitic and oleic acids, which are the most common; with more complex mixtures it does not give satisfactory results.[2]

**3. Determination of the Stearic and Palmitic Acids.**—With a mixture of solid fatty acids free from liquid acids and composed, as is the

[1] *Rend. Soc. chim. ital.*, 1912, p. 51.

[2] On the solubility of the various acids in alcohol, see also a paper by Kreis and Hafner in *Zeit. Unt. Nahr. und Genussmittel*, 1903, p. 22, and also papers by Heiduschka and Burger and by Serger in *Zeits. für öffent. Chem.*, 1913, pp. 87 and 131.

more general case, of stearic and palmitic acids, the respective proportions of these two acids may be determined from either the acid number or the melting point of the mixture.

The following table of Mangold and Marazza gives the proportions of stearic and palmitic acids in a mixture of the two acids, on the basis of the acid number.

TABLE XLII

**Stearic and Palmitic Acids from the Acid Number**

| Acid Number (mgrms. of KOH per gram of mixture). | 100 parts of mixture contain | | Acid Number (mgrms. of KOH per gram of mixture). | 100 parts of mixture contain | |
|---|---|---|---|---|---|
| | Stearic Acid. | Palmitic Acid. | | Stearic Acid. | Palmitic Acid. |
| 197·50 | 100 | — | 208·86 | 45 | 55 |
| 198·50 | 95 | 5 | 209·95 | 40 | 60 |
| 199·50 | 90 | 10 | 211·06 | 35 | 65 |
| 200·50 | 85 | 15 | 212·18 | 30 | 70 |
| 201·50 | 80 | 20 | 213·30 | 25 | 75 |
| 202·50 | 75 | 25 | 214·45 | 20 | 80 |
| 203·50 | 70 | 30 | 215·60 | 15 | 85 |
| 204·60 | 65 | 35 | 216·77 | 10 | 90 |
| 205·60 | 60 | 40 | 217·95 | 5 | 95 |
| 206·70 | 55 | 45 | 219·13 | 0 | 100 |
| 207·77 | 50 | 50 | | | |

The following table gives the stearic and palmitic acids contained in a mixture of these two acids in relation to the melting point of the mixture, according to Heintz and according to Hehner.

TABLE XLIII

**Palmitic and Stearic Acids from the Melting Point**

| Melting Point. | | Solidifying Point. | Palmitic Acid. % | Stearic Acid. % |
|---|---|---|---|---|
| Heintz. | Hehner. | | | |
| 62·0° | 61·8° | — | 100 | 0 |
| 60·1 | 59·0 | 54·5° | 90 | 10 |
| 57·5 | 56·5 | 53·8 | 80 | 20 |
| 55·1 | 54·2 | 54·0 | 70 | 30 |
| 56·3 | 55·5 | 54·5 | 60 | 40 |
| 56·6 | 55·6 | 55·0 | 50 | 50 |
| 60·3 | 59·4 | 56·5 | 40 | 60 |
| 62·9 | 61·5 | 59·3 | 30 | 70 |
| 65·3 | 64·2 | 60·3 | 20 | 80 |
| 67·2 | 66·5 | 62·5 | 10 | 90 |
| 69·2 | 68·5 | — | — | 100 |

## 19. Unsaponifiable Substances

By unsaponifiable substances in fatty matters is usually meant both substances which are not attacked by the alkali during the saponification, such as mineral oils, resin oils, solid paraffin and ceresine—which are unsaponifiable in the strict meaning of the term—and also substances which are liberated by the saponification itself and separate owing to their slight solubility under the conditions of saponification, such being, for instance, the higher alcohols (ceryl and myricyl alcohols, cholesterol and phytosterol).

The latter substances form an integral part, i.e., enter into the constitution, of many fatty matters and waxes, while the former (mineral oils and the like) may be added artificially to fats.

To separate the unsaponifiable substances from fats it suffices to saponify in the usual way (*see* 5), to dissolve the soap in water and shake the solution with ether or petroleum ether (b.pt. below 80°), to separate the two liquids and evaporate the ethereal solution, which will leave the unsaponifiable matters. To prevent emulsification, which often occurs when an alkali soap is shaken with ether, a little alcohol may be added and a larger quantity of ether used.

To determine quantitatively the unsaponifiable substances, it is more convenient and accurate to work as follows:

20 grams of the substance to be examined are saponified by boiling with 15 c.c. of 50% caustic soda solution and 50 c.c. of 95% alcohol for about 30 minutes, the liquid being then transferred to a dish and the alcohol evaporated, 8-10 grams of sodium bicarbonate (to transform the excess of caustic alkali into carbonate) and 70–80 grams of siliceous sand being gradually mixed in. When the whole is quite dry it is placed in a thick filter-paper thimble and extracted in an extraction apparatus with petroleum ether (b.pt. below 80°). The solvent is subsequently extracted, the residue, dried at 100° and weighed, giving the quantity of unsaponifiable matter.

The unsaponifiable matters which may be extracted from fats in this way or by the other methods given under particular cases (*see* Tallow, 3, Detection of Phytosterol) are mainly as follows:

**1. Higher Alcohols.**—These are divided into those of the aliphatic series (cetyl, ceryl, myricyl) and those of the aromatic series (cholesterol, phytosterol). The former, which occur especially in waxes, are solid and melt at moderately high temperatures—cetyl alcohol at 50°, ceryl at 79° and myricyl at 85°; they are soluble in alcohol, from which they crystallise readily, and they dissolve in and combine with boiling acetic anhydride, the solution remaining liquid on cooling provided that a sufficient excess of acetic anhydride were used.

The aromatic higher alcohols are found in almost all fats, although often in very small proportions.

*Cholesterol* occurs in fats of animal origin. It is soluble in hot alcohol, from which it crystallises, on cooling, in nacreous leaflets having the appearance of rhombic plates under the microscope (Fig. 54). It melts at 145–150° and dissolves in boiling acetic anhydride, the cold solution depositing a

solid acetyl compound which, when purified and recrystallised from alcohol, melts at 114-115°. If a solution of a little cholesterol in 2 c.c. of chloroform is shaken with an equal volume of concentrated sulphuric acid, the chloroform solution assumes a red coloration, which soon changes to cherry-red and then to violet-red, this persisting for some days, whilst the acid liquid turns reddish brown; if a few drops of the chloroform solution are shaken in a porcelain dish, the colour changes successively to blue, green and dirty yellow.

FIG. 54

*Phytosterol* or *sitosterol* (*cholesterol from plants*) occurs in fatty substances of vegetable origin. It dissolves in alcohol, from which it crystallises in tufts of broad, blunt-ended needles, having the microscopic appearance of elongated, blunted plates (Fig. 55), m.pt. 135–144°. When boiled with acetic anhydride, phytosterol also gives an acetyl-compound, m.pt. 125–137° (purified and recrystallised). With chloroform and sulphuric acid it behaves like cholesterol.

FIG. 55

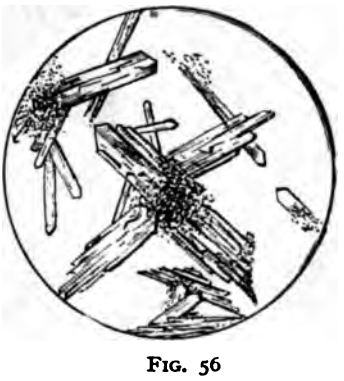

FIG. 56

When a mixture of cholesterol and phytosterol—which may be obtained from a mixture of animal and vegetable fats or oils—is crystallised from alcohol, the crystals show the predominant form of the phytosterol (Fig. 56) and melt at temperatures intermediate to the melting points of cholesterol and phytosterol (*see also* Lard).

**2. Paraffin Wax. Ceresine.**—These are solid and are insoluble in alcohol, aniline and acetic anhydride,[1] and hence distinguishable from the higher alcohols.

**3. Mineral Oils, Tar Oils, Resin Oils.**—These are liquids and are readily recognisable by their appearance and odour. Resin oils are also characterised by their reaction with sulphuric acid (*see* Resin Oils) or by their rotatory power (+ 30° to + 50° in a 200 mm. tube), and the mineral oils

[1] If acetic anhydride is boiled for a long time with paraffin wax or ceresine, the latter dissolves, but the solution becomes turbid as soon as the flame is removed.

by their insolubility in alcohol or aniline, in which solvents tar oils and resin oils dissolve.

## 20. Detection and Determination of the Resin

Resin (colophony) [1] is often found mixed with fatty substances (especially boiled linseed oil for varnishes and the like), waxes, and particularly soaps.

**1. Qualitative Investigation.**—With neutral fats or oils, fatty acids, or waxes, 5–10 grams of the substance are heated to boiling for a few moments with as much 70% alcohol and the alcoholic liquid allowed to cool, filtered off and evaporated: the colophony, which is easily soluble in alcohol, remains as residue and is identifiable by its general characters and by means of the following reaction (Morawski's):

A small quantity of colophony, dissolved in 1–2 c.c. of acetic anhydride and then treated with 1–2 drops of sulphuric acid of D 1·53 (34·7 c.c. of sulphuric acid of 66° Baumé plus 35·7 c.c. of water), gives a transient, violet-red coloration.

A similar reaction is, however, given by cholesterol when, for instance, wool fat may be present. In such case the residue from the evaporation of the alcoholic liquid is taken up in dilute potassium hydroxide solution (which readily dissolves colophony), the liquid being shaken with ether (which dissolves cholesterol) and the aqueous alkaline liquid acidified and the resin acids thus obtained tested by means of Morawski's reaction.

With soap, about 5 grams are dissolved in water and the solution shaken with ether, the aqueous liquid being acidified and the fatty acids tested by Morawski's reaction.

**2. Quantitative Investigation.**—When mixed with fatty substances or with soaps, colophony may be determined by *Twitchell's method*, which is based on the fact that, in alcoholic solution, the acids of the resin are not esterified by gaseous hydrogen chloride, whilst fatty acids are readily converted into ethyl esters under these conditions. The procedure is as follows:

The mixture of fats and resin is saponified in the usual way and the fatty acids then separated by acidifying the soap solution. In the case of a soap, this is dissolved in water and the solution filtered and then decomposed by acid. With mixtures containing unsaponifiable substances it is necessary, after saponification, to extract the liquid with benzene or petroleum ether to remove the unsaponifiable matter, the aqueous solution being then decomposed with an acid. The fatty and resin acids thus obtained are well washed and dried and 2–3 grams dissolved in 50 c.c. of absolute alcohol and dry hydrogen chloride gas passed into the solution kept at about 10° by immersion in water and ice. The current of gas is stopped after 1½ hour, when the saponification is complete. After an hour's rest, the liquid is diluted with 5 vols. of water and boiled until the esters, mixed with resin acids, float in a clear layer and the alcohol is then eliminated.

The resin acids may then be determined either volumetrically or gravimetrically.

[1] For its characters, *see Colophony*, Vol. II, Chapter IX.

(a) *Volumetrically.* The product of the esterification is dissolved in ether and washed repeatedly with water to eliminate the mineral acid and then diluted with 50 c.c. of neutral alcohol and titrated with N/10-potassium hydroxide in presence of phenolphthalein: 1 c.c. N/10-KOH = 0·0346 gram of resin.

(b) *Gravimetrically.* The esterification product is dissolved in 50 c.c. of petroleum ether (b.pt. below 80°), shaken well, and the aqueous acid liquid separated. The petroleum ether solution is washed with water and shaken with 50 c.c. of an aqueous solution containing 0·5 gram of caustic potash and 5 c.c. of alcohol. The resin acids pass into the aqueous alkaline solution, whilst the fatty esters remain dissolved in the petroleum ether. The alkaline aqueous liquid is, therefore, separated and acidified, the resin acids thus obtained being removed by shaking the liquid with ether; the solvent is then evaporated and the residue dried at 100° and weighed.

This method gives only approximately exact results, which are more accurate with the volumetric than with the gravimetric method. Modifications have been suggested by Fahrion [1] and by Wolff and Scholtze,[2] but it is most commonly used in its original form. For more exact determinations, the method of Twitchell and Gladding may be used under the conditions laid down by Holde and Marcusson.[3] Another method for the determination of resin, based on the solubility of the alkali resinates in acetone, has been proposed by Leiste and Stiepel.[4]

## 21. Maumené Number

This represents the rise in temperature produced when the fatty substance is mixed with concentrated sulphuric acid under definite conditions. Various methods of measuring this increase, based on the original one of Maumené, have been suggested. Nowadays suitable forms of apparatus are used (*thermo-oleometers*), such as that of Jean[5] or that of Tortelli.

*Tortelli's thermo-oleometer* consists of a small glass vacuum-jacketed vessel *A* (Fig. 57), and a thermometer-stirrer *B* provided with two glass vanes near the bulb. 20 c.c. of the oil are pipetted into *A*, stirred for a minute by rotation of the stirrer and the temperature read (*t*). By means of another pipette 5 c.c. of sulphuric acid (D exactly 1·8413) are allowed to flow on to the oil while the stirrer is rotated rapidly backwards and forwards and kept just in contact with the bottom of the vessel. The stirring is continued until the

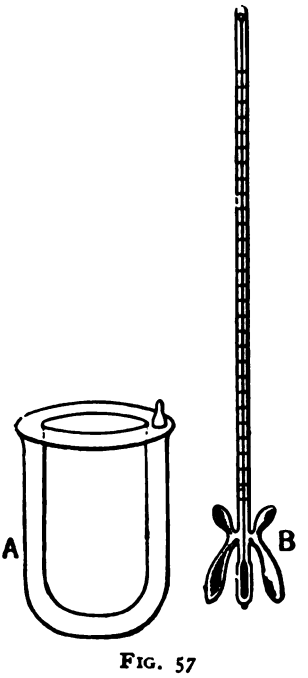

FIG. 57

[1] *Chem. Rev. Fett. Ind.*, 1911, p. 239.
[2] *Chem. Zeit.*, 1914, p. 369.
[3] *Mitt. aus. dem Kgl. Materialpr. Amt.*, 1902, p. 40.
[4] *Chem. Zentralbl.*, 1914, I, p. 577.
[5] *See* F. Jean: *Chimie analytique des matières grasses.*

temperature reaches a maximum ($t_1$) and remains there for a few minutes. The Maumené number is $t_1 - t$.

To obtain constant and comparable results it is necessary to operate always exactly as described and to use acid of the exact density ; this may be controlled by using 20 c.c. of distilled water in place of the oil, the value 50 being then obtained by the test. The oil and acid used must be left for some time (about 30 minutes) to attain the temperature of the surrounding air.

In the case of a drying oil, it is convenient to dilute the oil suitably with olive oil of a known Maumené value, the result obtained being then properly corrected.

Solid fats are used in the fused state, the acid being at the ordinary temperature ; allowance is then made in the calculation for the respective specific heats.

The results obtained for drying and non-drying oils with Tortelli's apparatus are about 8–10 higher than those given by Jean's apparatus.

The results vary with the method used for their determination and with the nature of the substances themselves. In general, however, drying oils, fish oils and fish-liver oils give values above 100, semi- and non-drying oils and blubber oils, values less than 100 (usually 30–90), and animal fats low values (30–35).

Old or rancid oils and those which have been exposed to the air or heated give values different from the fresh oils.

## 22. Drying Properties of Oils

Certain fixed oils, when exposed to the action of the air, thicken and gradually dry, forming transparent and elastic pellicles like rubber. Such oils are described as *drying oils*. Oils which either remain fluid or thicken but little, even after long exposure to the air, are *non-drying* and those which thicken and dry, although incompletely and slowly, are termed *semi-drying*.

The drying properties of an oil depend on its power to absorb, with greater or less rapidity, atmospheric oxygen, so that the drying properties of an oil may be determined from the quantity of oxygen absorbed and from the rapidity of the absorption.

There are several methods of determining the absorption, the most common being those of Livache and Bishop.

1. LIVACHE'S METHOD. Precipitated lead is prepared by immersing a sheet of zinc in 10% lead acetate solution acidified with nitric acid, and washing the lead precipitate formed with water, alcohol and ether and drying it in a vacuum over sulphuric acid. A clock-glass with about 1 gram of the lead on it is weighed and about 0·5 gram of the oil allowed to fall in drops on to it, care being taken that the different drops do not unite. The glass is reweighed and then exposed to the air in a well-ventilated and lighted place at a constant temperature. It is weighed from time to time until no further increase occurs, the maximum increase representing the oxygen absorbed.

2. BISHOP'S METHOD. Pure manganese resinate is prepared by treating the commercial product with petroleum ether, filtering the solution, dis-

tilling the solvent, drying the residue on a water-bath and powdering it. Of this resinate, 0·2 gram is heated in a water-bath with 10 grams of the oil to be tested until completely dissolved. 1 gram of precipitated silica and a glass stirring-rod are placed in a dish and the whole tared, 1·02 gram of the oil plus resinate being allowed to fall drop by drop on to the sand and the whole weighed. The mass is well mixed and left exposed to the air at the temperature 17–25° for drying oils or 20–30° for other oils. After 6 hours and after further successive intervals of 12 hours the basin is weighed (the mass being stirred each time) until of constant weight. The maximal increase of weight, multiplied by 100, Bishop terms the *degree of oxidation* of the oil.

Drying oils usually absorb oxygen easily and rapidly, so that after an exposure of 2–3 days the absorption is practically at the maximum attainable even after 8–10 days. On the other hand, non-drying oils do not increase in weight during the first days of exposure and begin to absorb a small quantity of oxygen only after 5–6 days.

According to Livache, the maximum amount of oxygen absorbed per 100 parts of linseed oil is about 14, the amounts for walnut oil, poppyseed oil, cottonseed oil and beechnut oil being 8–5. Olive, arachis, sesamé and colza oils absorb only 1–3% of oxygen.

According to Bishop's method, the mean degree of oxidation is 17 for linseed oil, 13–15 for hempseed, poppyseed and walnut oils, and 6–9 for cottonseed, sesamé and arachis oils.

## 23. Colour Reactions.

Different fatty substances, more particularly the fatty oils, give special colorations with various reagents, such as acids, alkalies and different salts. Some of these reactions serve to distinguish certain groups of oils, whilst others, being specific for a single oil, serve to characterise the latter. These specific reactions will be dealt with in the special part in the paragraphs treating of the particular oils (*see* Cottonseed Oil, Sesamé Oil). Some of the group reactions in more general use for the distinction of the different groups of vegetable oils (for animal oils, *see* Fish Oils) will be described here.

1. HEYDENREICH'S REACTION. Five or six drops of the oil are allowed to drop from a pipette on to about 5 c.c. of pure sulphuric acid (66° Baumé) in a flat-bottomed porcelain dish. In about three minutes the oil spreads to form a very thin layer on the acid; the colour formed during this time in the zone of contact between oil and acid is observed.

With olive, arachis and almond oils, there is no sensible change of colour, the oil remaining pale yellow or yellow, although sometimes with olive oil a greenish-yellow coloration appears. With very old or rancid oils, colours tending to orange or brown may be formed.

Semi-drying oils give orange or brown colorations, and drying oils brown or black colorations, while the oil forms a thick skin (*see also* under the separate oils).

2. HAUCHECORNE'S REACTION. 6 c.c. of the oil are vigorously shaken in a test-tube with 2 c.c. of nitric acid prepared from 3 vols. of pure nitric acid of 40° Baumé and 1 vol. of water. Note is made of the coloration

assumed by the oil after shaking for about two minutes and of its coloration after the mixture has been kept for 20 minutes in a boiling water-bath.

Olive, almond, hazel-nut and arachis oils retain their natural colour or become somewhat paler. Olive oil may, however, sometimes assume a greenish tint, especially in the cold. If these oils are rancid, they may turn orange-coloured.

Sesamé, cottonseed, beechnut, linseed, walnut, colza, and mustard oils, etc., change to orange or brownish red.

3. BRULLÉ'S REACTION. In a test-tube 10 c.c. of the oil, 0·1 gram of dry, finely powdered egg-albumin and 2 c.c. of pure nitric acid prepared as for Hauchecorne's reaction are carefully and uniformly heated until the acid begins to boil, the whole being then shaken somewhat and the heating continued until the albumin is completely dissolved, this occurring in a few seconds.

During the boiling with the acid and albumin, olive oil becomes almost entirely decolorised and after cooling forms a more or less turbid liquid of a straw-yellow colour which persists for a long time, but after 24 hours it sets to a solid mass of the same colour. Similar behaviour is shown by arachis, almond and walnut oils.

Seed-oils, however, become deep yellow (colza, sesamé) or orange-red to brown (cottonseed, poppyseed, maize, beechnut, linseed, etc.).

4. BELLIER'S REACTION. 5 c.c. of the oil or filtered fused fat, 5 c.c. of pure, colourless nitric acid of D = 1·4 and 5 c.c. of a cold, saturated solution of resorcinol in benzene are introduced into a graduated cylinder with a ground stopper and shaken for about 10 seconds, the colour being observed during the shaking and immediately afterwards (10–15 seconds).

In place of the benzene solution of resorcinol, a 0·1% ethereal solution of phloroglucinol (*Kreis*) may be used.

Seed oils in general, and especially sesamé, cottonseed, poppyseed, linseed, maize (corn oil), soja-bean and colza oils, give colorations varying from pink to red to violet to brown (with phloroglucinol more distinctly red).

This reaction serves more particularly to detect vegetable seed oils in animal fats (lard), in lard oil, in foot oils, and also in olive oil, since these animal fats and oils and olive oil give no appreciable coloration, at any rate within 5–20 seconds. After this time all oils and fats give colorations.

Practice with oils and fats of known origin is necessary in order to distinguish pure oils and fats from mixtures by this reaction.

With oils which have been subjected to long exposure to light or to heating in the air, the reaction fails.

## 24. Elaidin Test

10 grams of the oil and 5 c.c. of nitric acid (D 1·40) are shaken in a test-tube for two minutes, 1 gram of mercury being then added and dissolved by energetic shaking; the tube is then left at rest for about 30 minutes.

With pure olive oil a solid white or yellowish mass is obtained and similar behaviour is shown by arachis, almond and lard oils. Sheep's foot oils, and mustard, colza, ravison, sesamé, cottonseed and other semi-drying

oils and oils of marine animals give a more or less semi-solid or pasty, coloured mass. Drying oils give an orange-yellow or brown liquid product.

# SPECIAL PART

# Vegetable Oils

By vegetable oils is meant those fatty substances extracted from the vegetable kingdom and liquid at the ordinary temperature. These oils are fairly numerous but only relatively few are in common use, these including olive, almond, arachis, colza, cottonseed, linseed, sesamé and castor oils, which are treated in detail below. Table XLIV on p. 410 gives the principal characters of these oils and of the other more important vegetable oils.

## ARACHIS OIL

From the seeds of *Arachis hypogœa*. It is pale yellow and has a slight odour and an agreeable taste. About 15 grams dissolve in 1000 c.c. of absolute alcohol at 15°.

With Heydenreich's, Brullé's and Hauchecorne's reagents it gives no appreciable colorations, only a pale pink colour being obtained with the last in the cold. The other chief physical and chemical characters are given later in Table XLIV.

Characteristic of arachis oil is its content of arachidic and lignoceric acids. The detection and, if required, the determination of these acids serves to identify the oil and to detect its presence (approximately also the quantity) in mixtures with other oils.

**1. Detection and Determination of Arachidic and Lignoceric Acids.**—The most convenient method for this purpose is that of Tortelli and Ruggeri (*see* below), which, like various other methods, is based on the same principle as Renard's older method.[1]

A preliminary and more rapid examination may be made by the other two methods described below.

1. TORTELLI AND RUGGERI. 20 grams of the oil are saponified, the fatty acids separated, and the solid acids extracted from these by means of the lead salts,[2] the operations being carried out exactly as described in general method 18 (Tortelli and Ruggeri's method). The solid fatty acids thus obtained are placed in a suitable flask, 100 c.c. of 90% alcohol and a drop of dilute hydrochloric acid (about normal) being added. The flask is closed with a stopper through which a thermometer passes into the liquid and is then heated gently (not above 60°) on a water-bath and carefully

[1] Among other methods suggested for the detection of arachis oil mention may be made of Torrini's modification of Blarez's method (*Ann. Lab. chim. centrale Gabelle*, Vol. VI, p. 513).

[2] According to Guarnieri, the preparation of the lead salts may be shortened by saponifying the oil with a concentrated solution of caustic potash in glycerine and then precipitating the lead salt with a solution of lead acetate in glycerine (*Staz. sper. agr. ital.*, 1909, p. 408).

shaken until a clear solution is obtained, this being allowed to cool. When the temperature has fallen somewhat, slender silvery needles begin to form and rapidly collect into tufts (lignoceric acid), together with gradually increasing shining, nacreous leaflets (arachidic acid). With the fatty acids from pure arachis oil, the temperature at which crystals begin to form as the alcoholic solution cools is 35–38°. The melting point of the mixture of acids obtained in this first crystallisation is usually 71-73°.

No other oil gives a crystalline precipitate in such conditions, even when the alcoholic solution of its solid acids (prepared as above) is cooled to the ordinary temperature. Only cottonseed oil and some olive oil from Tunisian olives give a precipitate, but this is amorphous and granular and in perfectly opaque mammillary masses, m.p. below 70°; further, such precipitate does not form in a second crystallisation.

If it is required to estimate exactly the *quantity* of arachidic and lignoceric acids, the crystals formed in the alcoholic solution are collected and washed with three successive quantities of 10 c.c. of 90% alcohol and then thoroughly with 70% alcohol. The crystals are then redissolved in 100 c.c. of 90% alcohol (or a less volume if the amount is small) and the crystallisation repeated as described above. The crystals thus obtained are collected on a filter, washed twice with 10 c.c. of 90% alcohol and then with 70% alcohol until this dissolves no more; they are then dissolved in a little boiling absolute alcohol, the solution being evaporated in a tared dish and the residue dried at 100° for about an hour and weighed.[1] To the weight found is added that of the arachidic and lignoceric acids remaining in solution in the 90% alcohol used for the various crystallisations and washings, the following solubility coefficients (Tortelli and Ruggeri) being employed:

| Weight of Acid obtained in grams. | Number of grams dissolved by 100 c.c. of 90% alcohol at a temperature of | | |
|---|---|---|---|
| | 15° | 17·5° | 20° |
| 1·00 or more . . | 0·071 | 0·081 | 0·091 |
| 0·70 . . . . . | 0·068 | 0·078 | 0·089 |
| 0·50 . . . . . | 0·064 | 0·075 | 0·084 |
| 0·25 . . . . . | 0·052 | 0·060 | 0·067 |
| 0·05 or less . . | 0·031 | 0·040 | 0·045 |

Arachis oil contains, on the average, 4·80% of arachidic and lignoceric acids together, so that the proportion of these acids found by the above method indicates if the oil is pure or not. Further, the presence and quantity of these acids serve for the characterisation and determination of arachis oil in mixtures with olive and other oils. In such mixtures, the crystallisation of the arachidic and lignoceric acids from the alcoholic solution of the solid fatty acids takes place at lower and lower temperatures as the proportion of arachis oil in the mixture diminishes.

[1] The mixture of arachidic and lignoceric acids thus obtained should melt at 74–75·5°.

The content of arachis oil in the mixture may also be deduced approximately from the temperature at which the first crystals form :

| Temperature of initial precipitation . . | 35–38° | 31–33° | 28–30° | 25–26° | 22–24° | 20–22° | 18–20° | 16–17° |
|---|---|---|---|---|---|---|---|---|
| Proportion of arachis oil . . | 100% | 60% | 50% | 40% | 30% | 20% | 10% | 5% |

The proportion of arachis oil in a mixture may, however, be determined more exactly from the quantitative determination of the arachidic and lignoceric acids, the content in the pure oil being 4·80%. In this way as little as 5% of arachis oil in admixture with other oils may be detected.

2. BELLIER'S METHOD (modified).[1] Into a conical flask of about 100 c.c. capacity are pipetted 1 c.c. of the oil and 5 c.c. of about 8% alcoholic caustic potash solution (80 grams of pure potassium hydroxide dissolved in 80 c.c. of water and made up to 1 litre with 90% alcohol). The flask is closed with a stopper carrying a tube 80 cm. long (to avoid loss of alcohol) and heated on a boiling water-bath with continual shaking until saponification is complete (4–5 minutes). The liquid is then cooled to about 25° and shaken with 1·5 c.c. (exactly) of dilute acetic acid (1 vol. of glacial acetic acid + 2 vols. of water), 3 drops (not more) of glacial acetic acid and 50 c.c. of 70% alcohol. If the liquid becomes turbid (as usually happens if arachis oil is present in marked quantity), it is gently heated until clear, the flask being then closed with a stopper through which passes a thermometer with its bulb in the liquid. The flask is then cooled and shaken in a water-bath so that the temperature of the liquid becomes exactly 16°, at which it is maintained for 5 minutes with gentle shaking.

If the liquid remains clear it is kept at 15·5° for 5 minutes, and if it still remains clear, arachis oil is either absent or present in less proportion than 5%. The appearance of turbidity at 15·5° indicates the presence of arachis oil (about 5%) in the oil. With higher proportions, marked turbidity occurs even at 16°. With pure arachis oil, the liquid begins to show turbidity at about 40°.

The temperature at which the alcoholic solution of the fatty acids, obtained as described above, first becomes turbid serves to indicate approximately the proportion of arachis oil in its mixtures with olive oil :

| | Temperature at which turbidity appears. |
|---|---|
| Pure olive oil . . . . . | 11·5–14·5° |
| ,, ,, + 5% arachis oil . . . . | 16–17 |
| ,, ,, 10 ,, . . . . | 19–20 |
| ,, ,, 20 ,, . . . . | 25–26 |
| ,, ,, 30 ,, . . . . | 29–30 |
| ,, ,, 40 ,, . . . . | 31–32 |
| ,, ,, 50 ,, . . . . | 33–34 |
| ,, ,, 60 ,, . . . . | 35–36 |
| ,, ,, 70 ,, . . . . | 36–37 |
| ,, ,, 80 ,, . . . . | 38 |
| ,, ,, 90 ,, . . . . | 39 |
| Pure arachis oil . . . . . | 40 |

[1] The modifications of Bellier's original method (*Ann. de Chim. analyt.*, 1899, 4) are due principally to Mansfeld (*Z. Unt. Nahr. Genussm.*, 1905, XVII, p. 57), Adler (*ibid.*, 1912, XXIII, p. 676), Luers (*ibid.*, 1912, XXIV, p. 683), and Evers (*Analyst*, 1912, p. 487).

3. FACHINI AND DORTA'S METHOD.[1]—This is based on the insolubility in acetone of the potassium salts of the solid fatty acids.

10 grams of the fatty acids obtained from the oil in the usual way are dissolved in 90 c.c. of pure, boiling acetone, the boiling solution being treated with 10 c.c. of aqueous N-caustic potash solution and allowed to cool to about 15°. The precipitate formed is collected on a dry filter, freed from liquid by suction, washed with small portions of pure acetone and then decomposed with a dilute acid to liberate the fatty acids, which are dissolved in petroleum ether. The solution is filtered and evaporated and the arachidic and lignoceric acids investigated by precipitation from 90% alcohol in the manner of the Tortelli and Ruggeri method.

**2. Detection of Adulterations.**—Commercial arachis oil may be adulterated with, or may contain as impurities, sesamé, cottonseed, colza, poppyseed and other seed oils. Sesamé and cottonseed oils are detected by the reactions of Villavecchia and Fabris and of Halphen (*see* Sesamé Oil and Cottonseed Oil), colza oil by Tortelli and Fortini's reaction and by a lowering of the saponification number (*see* Colza Oil), poppyseed oil and other seed oils in general by the colour reactions of Heydenreich, Hauchecorne, and Brullé, and by a diminution in the content of arachidic and lignoceric acids.

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*Comestible arachis oil*, when fresh, should contain only traces of free acids. Old oils and those for industrial use are more or less acid and may contain up to about 30% of free acid (calculated as oleic acid), the usual proportion being about 20%. *Arachis oil for soapmaking* should contain not more than 1% of moisture and foreign matters together and should have $D = 0{\cdot}919$–$0{\cdot}921$, iodine number 87–100, solidification point of the fatty acids 28–32·5°, Maumené number (Tortelli) 50·6.

The following products are also sold: *Arachis margarine*, produced by pressing the oil in the cold (m.pt. 22–25°, iodine number 79–80), *arachis grease*, produced by purifying the rancid oil with soda and composed of sodium soap, neutral oil and various impurities; and *arachis oil No. 2*, obtained by the purification of rancid oils with ammonia. The commercial value of the grease and of the oil No. 2 depends on the content of total fatty matter (*see* General Part, 1, *A* and *C*).

## COLZA OIL AND OTHER CRUCIFEROUS OILS.

The more common oils of the Cruciferæ are colza and ravison oils; less common are those of jambo, turnip, mustard (white and black), radish seed and hedge mustard. All have very similar characters and properties.

Colza oil and ravison oil (from the seeds of *Brassica campestris* and *B. napus*), which are most used, are yellow, sometimes tending to brown; they have a special, more or less pronounced odour and a slightly acid taste. About 8 grams dissolved in 1000 c.c. of absolute alcohol at 15°. Their characters are given later in Table XLIV.

With Heydenreich's reagent they give orange colorations with fairly apparent brown striæ, especially if the containing dish is moved slowly. With Hauchecorne's and Brullé's reagents they give more or less deep orange colorations.

[1] *Rend. Soc. chim. ital.*, 1910, p. 248, and 1912, p. 51; *Chem. Zeit.*, 1914, p. 18.

Characteristic of colza and ravison oils, and of those of the other Cruciferæ mentioned above, are their low saponification number (*see* Table XLIV) and their content of erucic acid. By the determination of the saponification number and essentially by certain tests on the fatty acids these oils may be identified and their presence in mixtures with other oils detected. These tests are as follows.[1]

**1. The Tortelli and Fortini Tests on the Fatty Acids.**—These tests include the determinations of the melting point and iodine number of the solid fatty acids and the critical solubility temperature of the sodium soap of the liquid acids, these characters being especially influenced by the presence of erucic acid. The solid and liquid fatty acids should first be prepared (*see* a) and the determinations indicated then made (*see* b and c).

(a) *Preparation of the solid and liquid fatty acids.* 20 grams of the oil are saponified with alcoholic potash and the potassium soap converted into the lead soap by the Tortelli and Ruggeri method (*see* General Methods, 18, 1). The lead soap, dried with filter-paper, is taken up with 80 c.c. of ether, shaken well, heated for 20–30 minutes in a reflux apparatus with occasional shaking and then cooled in water at 15° for an hour. The ethereal liquid is subsequently decanted through a filter into a separating funnel, as little as possible of the solid residue being introduced on to the filter. The residue is heated with 40 c.c. of ether in a reflux apparatus for 20 minutes, cooled at 15° for an hour, and the whole then collected on the filter, the filtrate passing into the separating funnel. The flask and residue are washed with 40 c.c. of ether. This washed lead soap, insoluble in ether, is introduced into another separating funnel by perforating the filter and washing down with ether, of which 100 c.c. are used.

To each separating funnel 150 c.c. of 20% hydrochloric acid are added, the funnel being thoroughly shaken and then left at rest until the ethereal layer has separated well, the aqueous liquid and the lead chloride formed being run off. This treatment is repeated with a second quantity of 100 c.c. of hydrochloric acid and if necessary with a third quantity. The two ethereal solutions are then washed twice with 100–150 c.c. of water, care being taken not to shake too vigorously. The ethereal solutions are finally filtered through two pleated filter-papers into two glass dishes, from which the solvent is evaporated at as low a temperature as possible. In one dish the solid acids (from the lead salts insoluble in ether) and in the other the liquid acids of the oil remain.

(b) *Tests on the solid acids.* The *melting point* is determined with a bulb tube (*see* General Part, 4) and is taken as that temperature at which the substance falls into the lower part of the bulb. The *iodine number* is determined by Hübl's method.

The solid fatty acids of pure colza oil melt at 41–42° and have the iodine number 62 : those of other seed oils and of olive oil melt at higher temperatures and have lower iodine numbers (*see* later).

(c) *Tests on the liquid acids.* The sodium soap of these is prepared and

[1] Use may also be made with advantage of Holde and Marcusson's method (*Zeitschr. für angew. Chem.*, 1910, p. 1260), which is based on the solubility of erucic acid in alcohol at a low temperature.

its *critical solubility temperature* in alcohol determined. For this purpose the liquid acids are dissolved in 40 c.c. of absolute alcohol, the solution being heated gently, treated with slight excess of saturated sodium carbonate solution, evaporated almost to dryness and dried in a vacuum over sulphuric acid. The dry residue is powdered and purified from the excess of admixed sodium carbonate by successive treatments with 50, 40 and 30 c.c. of absolute alcohol, with which it is heated to boiling on a water-bath. The liquids are filtered hot and the sodium soap separated by cooling as a white or straw-yellow, caseous mass, which is pumped off and dried in a vacuum over sulphuric acid. Of the perfectly dry, powdered sodium soap, 0·5 gram is treated in a large test-tube with 20 c.c. of absolute alcohol, the tube being hung in a beaker full of water and a thermometer introduced so that its bulb is in the centre of the liquid.

The liquid is then heated and continually stirred with the thermometer until a clear solution is obtained, the whole being then allowed to cool spontaneously. At a certain point the alcoholic solution in the test-tube is seen to contain minute crystals, which are only barely noticeable at first, but rapidly multiply and fill the whole mass of the liquid. The temperature at which the first crystals are observed is the characteristic critical temperature.

When the crystallisation is well under way, the thermometric column remains stationary for some time, or at least falls with greatly increased slowness.

The sodium soap of the liquid fatty acids of colza oil has the critical solubility temperature in alcohol, 50–45°; for other seed oils and for olive oil this temperature is lower (*see* later). Further, the sodium soaps of olive oil and of various seed oils are deposited with a caseous, flocculent and glutinous appearance, whereas that of olive oil, at least at first, is distinctly crystalline.

From the melting point and iodine number of the solid fatty acids and the critical solubility temperature of the sodium soap of the liquid acids, colza (or ravison) oil may be detected and approximately estimated in its mixtures with other oils; the following data are given by Tortelli and Fortini:

| Oils. | Melting Point of Solid Acids. | Iodine Number of Solid Acids. | Critical Solubility Temperature of the Sodium Soap of the Liquid Acids. |
|---|---|---|---|
| Colza oil | 41–42° | 62 | 50–45° |
| Olive oil | 58–59 | 7·8 | 24–20 |
| Colza oil, 50 / Olive oil, 50 | 47–48 | 32 | 40–35 |
| Colza oil, 30 / Olive oil, 70 | 48–49 | 28 | 35–30 |
| Colza oil, 20 / Olive oil, 80 | 50–51 | 22 | 35–30 |
| Colza oil, 10 / Olive oil, 90 | 54–55 | 12·8 | 34–30 |
| Sesamé oil | 55–56 | 9·2 | 20–18 |
| Arachis oil | 57–58 | 13 | 22–18 |
| Cottonseed oil | 57–58 | 19 | 16–14 |

**2. Detection of Adulterations.**—Colza and ravison oils may be found mixed with olive oil (*q.v.*) and, in their turn, may be adulterated with other seed oils (linseed, poppyseed, cameline, hempseed, etc.), and particularly with fish oils and oils of other marine animals, as well as with mineral oils.

The determination of the various characters (especially saponification, iodine and Maumené numbers) and the test for erucic acid by Tortelli and Fortini's method readily show if the oil is pure or otherwise. Seed oils in general and animal oils raise the saponification number, while linseed, hempseed and poppyseed oils raise also the iodine and Maumené numbers. Fish oils and other marine animal oils are detected by means of the test for the octabromo-compounds and the Tortelli and Jaffe reaction (*see* Fish Oils), and mineral oils by testing for unsaponifiable substances.

***

*Colza oil for comestible and illuminating purposes* should be well refined and not acid. *Industrial ravison oil* should have : D = 0·911–0·937, iodine number = 103–108, saponification number = 175–178, refractive index (Zeiss) at 25° = 68–71, Maumené number (Tortelli) = 60·8°.

## COTTONSEED OIL

Obtained from the seeds of *Gossypium herbaceum*. It is yellow or golden-yellow or, if not well refined, slightly reddish-yellow ; it has characteristic but not very pronounced smell and taste. About 18 grams dissolve in 1000 c.c. of absolute alcohol at 15°. The other physical and chemical characters are indicated in Table XLIV.

Heydenreich's reagent gives a deep orange, and Hauchecorne's or Brullé's reagent a reddish-brown, coloration with the oil. The latter also gives the following characteristic reactions :

**1. Milliau's Reaction, modified by Armani.**—10 grams of the oil are saponified in the usual way, the soap being dissolved in water and the solution shaken in a separating funnel with 100 c.c. of ether and 30 c.c. of 10% hydrochloric acid. After standing, the acid aqueous layer is removed and the ethereal solution of the fatty acids washed by shaking several times with water until the latter no longer gives an acid reaction. The ether is then evaporated, the fatty acids thus obtained being dissolved in 15 c.c. of 90% alcohol (puriss.) [1] and the solution mixed with 1–2 c.c. of alcoholic silver nitrate solution and heated in a water-bath at 80–90°.

Pure cottonseed oil gives an intense brown coloration almost immediately and then also a black precipitate. Mixtures of oils or fats containing cottonseed oil yield a violet-brown coloration which, after a few minutes' heating,

[1] This reaction and in general all reactions with silver nitrate require the use of very pure alcohol, which does not show the least brown coloration on protracted heating with silver nitrate. The absolute alcohol of commerce may be purified as follows (Tortelli and Ruggeri) : A litre of alcohol is heated for an hour in a reflux apparatus with 3 c.c. of 5% silver nitrate solution and then distilled. The distillate is treated with potassium permanganate until it assumes a persistent red colour and is then left for 24 hours with occasional shaking and subsequently filtered. The filtrate is treated with 2 grams of pure caustic potash, heated for an hour in a reflux apparatus and distilled, the distillate being diluted to the desired strength with distilled water.

becomes intense brown, a black precipitate also forming in some cases. Even with mixtures containing 1% of cottonseed oil a feeble brown coloration appears after 5–10 minutes of heating, whilst with oils and fats free from cottonseed oil no sensible coloration is ever formed.

**2. Milliau's Reaction, modified by Tortelli and Ruggeri.**—The liquid fatty acids are extracted from 20 grams of the oil by Tortelli and Ruggeri's lead-salt method (*see* General Methods, 18, 1) and 5 c.c. of them dissolved in a test-tube in 10 c.c. of 90% alcohol (puriss.), the solution being thoroughly mixed with 1 c.c. of 5% aqueous silver nitrate solution and heated in a water-bath at 70–80°.

With pure cottonseed oil the liquid assumes almost immediately a reddish coloration which soon turns to reddish-brown, the liquid then becoming turbid and appearing violet-blue in transmitted light; this happens after 5–10 minutes heating. With oils and fats quite free from cottonseed oil no coloration is obtained even after heating for half an hour. With mixtures containing only 1% of cottonseed oil, a deep brown colour soon appears.

**3. Halphen's Reaction.**—According to the most recent statement by the author,[1] this test is carried out as follows: In a test-tube are placed 1 c.c. of the oil and 2 c.c. of sulphocarbon reagent prepared by dissolving 1 gram of powdered, refined sulphur in 100 c.c. of carbon disulphide and then diluting with 100 c.c. of amyl alcohol. The tube is immersed to the extent of two-thirds in a salt solution and heated to boiling for an hour, 2 c.c. of the same reagent being then added and the heating continued for 30–40 minutes. In presence of cottonseed oil, a red, pink or orange-pink coloration—according to the proportion of cottonseed oil present (down to about 1% as a minimum)—appears more or less rapidly.

Water hinders the reaction, so that the test-tube should be thoroughly dry and the reagents and oil anhydrous; the latter is filtered through a double dry filter.

Some cottonseed oils which have undergone special treatments give, in place of a decided red coloration, a brown tint with an orange basis, this being well seen by looking through the whole depth of the liquid at a white ground.

With green or greenish olive oils containing little cottonseed oil, the reaction is uncertain; in such cases it is well to decolorise the oil beforehand by heating it at about 50° with animal charcoal and filtering at the same temperature.

**4. Halphen's Reaction, modified by Gastaldi.**—A test-tube containing 5 c.c. of the oil, 1 drop of pyridine and 4 c.c. of a 1% solution of sulphur in carbon disulphide is heated in a boiling water-bath for about 30–60 minutes. In presence of cottonseed oil a red, pink or yellowish-pink coloration—according to the amount of the cottonseed oil—is formed as with Halphen's reagent; the colour is more distinct and intense than with the latter and is visible even with 0·5% of cottonseed oil.

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Halphen's reaction and Gastaldi's modification of it fail with cottonseed oils which have been heated above 200° or subjected to prolonged treatment

[1] G. Halphen: *Huiles et Graisses végétales comestibles* (Paris, 1912), p. 340.

with sulphur dioxide or chlorine ; the reaction of the liquid fatty acids with silver nitrate (Tortelli and Ruggeri) is given, although in an attenuated form, by oils which have been heated to 250° for 10–20 minutes. This observation is, however, of little practical value, since cottonseed oil treated in this way is scarcely utilisable, at any rate for mixing with comestible olive oil.

It is also to be noted that kapok and baobab oils give the same reactions as cottonseed oil, both with silver nitrate and with the carbon disulphide reagent, but even far more intensely (with silver nitrate the reaction occurs even in the cold and with Halphen's reagent, 1% of kapok oil mixed with other oil gives almost the same coloration as pure cottonseed oil). Kapok oil may, according to Milliau,[1] be distinguished from cottonseed oil by means of the action of silver nitrate on the fatty acids in the cold ; but actually the fatty acids of cottonseed oil also slowly reduce silver nitrate in the cold and, in the case of mixtures, the reaction may be due as much to a little kapok oil as to a large amount of cottonseed oil. For a more certain indication other data must be employed. For instance, with mixtures of olive and arachis oils, the iodine number and other constants will show if the proportion of the extraneous oil is large or small. Thus, an arachis oil which gives Halphen's reaction as sharply and intensely as pure cottonseed oil but has a normal iodine number and a normal content of arachidic and lignoceric acids cannot possibly contain an amount of cottonseed oil capable of giving such an intense colour reaction ; it is, therefore, more probable that such an oil is contaminated with a little kapok oil than with much cottonseed oil.

***

*Comestible cottonseed oil* should show little colour and no unpleasant smell or taste and no acidity. The *industrial oil* should have : D = 0·922–0·930, iodine number = 103–110, solidification point of the fatty acids = 32–40°, Maumené number (Tortelli) = 78·8°.

*Refinery residues of cottonseed oil* (*soapstock*), which are pasty and brownish-yellow to black, are valued on the basis of their total content of fatty matter (standard 50%), for the determination of which, *see* General Part, 1, *A–C*.

*Cottonseed margarine* or *stearine* is the solid part which separates on cooling the oil and is recovered from the latter by pressure at 10–11° ; it is white or yellowish, has the consistency of butter (m.p. 16–32°) and gives the same colour reactions as cottonseed oil. Its specific gravity at 100° is 0·864–0·868, saponification number 194–195, iodine number 95–96. Its value depends on the titer (solidifying point of the fatty acids ; *see* Tallow) and on the content of total fatty matter (*see* General Part, 1, *A–C*).

## LINSEED OIL

Ordinary or crude linseed oil (for boiled linseed oil, *see* next chapter : Industrial Products of the Treatment of Fatty Matters), from the seeds of *Linum usitatissimum*, is yellow or brownish-yellow and has a peculiar odour and an unpleasant taste. It dissolves in about 40 parts of cold or 5 parts of boiling absolute alcohol. It contains a certain quantity of unsaponifiable substances (1–1·3%). Its physical and chemical characters are given in Table XLIV.

It is coloured deep orange with brown striæ by Heydenreich's reagent and soon sets to a black, tarry skin. By Hauchecorne's or Brullé's reagent it is coloured an intense brownish-red. Besides determinations of the

[1] *Ann. de chim. analyt.*, 1905, p. 9.

chemical and physical characters, the following special tests may be made on this oil:

**1. Reaction of the Hexabromo-compounds.**—When vigorously shaken in a stoppered cylinder with 100 c.c. of a mixture of 28 vols. of glacial acetic acid, 4 vols. of nitrobenzene and 1 vol. of bromine (*Halphen's bromine reagent*), 5 c.c. of the oil give a yellow precipitate composed of hexabromo-compounds of linolenic acid. This precipitate is soluble in boiling benzene and melts undecomposed at 175–180° (difference from oils of marine animals; *see* Fish Oils).

Drying walnut and hempseed oils behave like linseed oil, but other vegetable and animal oils (excepting those of marine animals) give no precipitate or only a slight turbidity with the bromine reagent.

**2. Drying Properties.**—Linseed oil, being a drying oil, readily absorbs oxygen, its drying power increasing with the rapidity with which it absorbs its maximum proportion of oxygen. Under the conditions of Livache's method (*see* General Methods, 22, Drying Properties of Oils), a good linseed oil absorbs about 14% of oxygen in two days, while by Bishop's method, the maximum is 17% and is reached in 24 hours.

**3. Detection of Adulterations.**—Linseed oil may be adulterated with other vegetable oils (especially colza, cottonseed, sesamé, poppyseed, cameline, hempseed and other drying oils) or with animal, mineral or resin oils, which are tested for as follows:

1. Other Vegetable Oils. Marked addition of other vegetable oils (especially if non-drying) to linseed oil generally lowers the iodine number and the Maumené number and a linseed oil with an iodine number below 165 and a Maumené number less than 120° is to be suspected. In particular, colza oil may be detected by the Tortelli and Fortini test, cottonseed oil by the Halphen and the silver nitrate reactions, and sesamé oil by the furfural reaction (*see* these oils). The presence of drying oils (poppyseed, cameline and the like) is moderately difficult to ascertain, since these oils do not possess special colour reactions.

2. Fish and other Marine Animal Oils. The presence of these oils may be detected by the Halphen and Marcusson octabromo-compound test and the Tortelli and Jaffe colour reaction (*see* Fish Oils).

3. Mineral Oils. These are detectable by the fact that they lower the density, the iodine number and the saponification number of linseed oil; they may, in addition, be tested for in the unsaponifiable part (*see* General Methods, 19, Unsaponifiable Substances).

4. Resin Oils. These may be recognised by the odour, by the colour reaction with sulphuric acid (*see* Resin Oils) and by the rotatory power (linseed oil is almost inactive, whereas resin oils are decidedly dextrorotatory); further, they increase the density and lower the iodine and saponification numbers.

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Free acids (calculated as oleic acid) up to 7% are allowable in linseed oil, unsaponifiable substances up to 1·5%, and moisture and various other impurities up to 1%. For the genuine oil, D = 0·930–0·934, iodine number = 164–191, Zeiss refractometric degree at 25° = 87·5, solidification point of the fatty acids = 13·3–20·6°.

## ALMOND OIL

This is obtained from the seeds of *Amygdalus communis* or ordinary almonds, the sweet and bitter varieties giving oils very similar in all their properties. Almond oil is yellow or golden-yellow and about 16 grams of it dissolve in 1000 c.c. of absolute alcohol.

With Heydenreich's, Hauchecorne's and Brullé's reagents i. remains pale yellow or becomes somewhat paler. The characters of the oil are given in Table XLIV and are determined by the methods already described.

**Detection of Adulterations.**—Almond oil may be adulterated with various seed oils (arachis, colza, cottonseed, walnut, sesamé, etc.), but especially with peach-kernel, apricot-kernel and plum-kernel oils. To detect such admixtures, the various characters must be determined (especially solidifying points of the oil and of the fatty acids, saponification and iodine numbers, Maumené number) and certain colour tests made (*see* below, 2).

The different extraneous oils may be detected as follows:

1. ARACHIS, SESAMÉ, COTTONSEED, COLZA, ETC. The first is detected by the arachidic and lignoceric acids, the second by the furfural reaction, the third by the Halphen reaction, and colza oil by tests on the fatty acids (*see* the respective oils). The presence of other seed oils in general (excluding those dealt with in 2) may be recognised by the colour reactions of Heydenreich, Hauchecorne, Brullé and Bellier (*see* General Methods, 23), to which almond oil does not sensibly respond.

2. PEACH-KERNEL, APRICOT-KERNEL AND PLUM-KERNEL OILS. These oils are commonly used as adulterants or substitutes for almond oil. They do not alter the characters of almond oil appreciably, excepting that apricot-kernel oil somewhat increases the Maumené number (50–51 for almond oil and 60–70° for apricot-kernel oil). The two following reactions serve for their detection.

*Bieber's reaction.* Equal volumes of pure sulphuric acid of 66° Baumé, concentrated nitric acid (D 1·42) and water are mixed, one vol. of such mixture being then shaken with 5 vols. of the oil in the cold. Pure almond oil forms a yellowish emulsion which becomes reddish only after some time. Apricot-, peach- and plum-kernel oils form emulsions of a transient purple colour, which soon changes to deep orange and then to brown.

*Reaction with nitric acid.* 1 c.c. of fuming nitric acid, 1 c.c. of water and 2 c.c. of the oil are shaken vigorously at a temperature of about 10°: pure almond oil yields a whitish emulsion which, in two or at most six hours, sets to a solid mass of compact white granules with a little colourless, supernatant liquid. In presence of apricot- or peach-kernel oil the emulsion becomes coloured, almost immediately, more or less reddish. If the solid mass and the liquid turn brown, the presence of other extraneous oils (colza) is demonstrated.

***

For medicinal uses, pharmacopœias prescribe the oil obtained by pressure from sweet almonds.

The *Official Italian Pharmacopœia* requires sweet almond oil to be clear,

highly mobile, yellow, almost odourless, and of sweetish taste : it should have D = 0·914–0·920, iodine number = 94–100, saponification number = 190–195, and should be incongealable at — 10° and should respond to the above reaction with nitric acid.

## OLIVE OIL

This is obtained from the fruit of *Olea europea*, and is pale yellow or sometimes greenish and with characteristic smell and taste ; about 15 grams of the oil dissolve in 1000 c.c. of absolute alcohol at 13–15°.

With Heydenreich's, Hauchecorne's, Brullé's or Bellier's reagent it gives a pale-yellow or greenish coloration, excepting with very old and rancid oils, which yield more or less deep orange tints. The characters of the oil are given in Table XLIV.

Olive oil may be adulterated with various seed oils, especially with arachis, cottonseed, sesamé, colza, ravison or soja-bean oil, and less frequently with maize, poppyseed and other oils. Adulteration with lard oil and with mineral oils has been observed, but only in exceptional cases.

**1. Tests and Determinations.**—Analysis of olive oil, with the aim of ascertaining the quality and purity, includes mainly the following :

(*a*) Examination of the objective properties, that is, the aspect (limpidity), colour, smell and taste. The odour is brought out well by rubbing a few drops of the oil between the hands and smelling the latter. The odour and taste indicate the fineness of an oil, its state of preservation and, with much practice, its purity.

(*b*) Determinations : solidifying point of the oil and the melting and solidifying points of its fatty acids ; the specific gravity ; the refraction on the Zeiss butyro-refractometer at 25° ; the Maumené number ; the acid, saponification and iodine numbers. All these are made by the methods described in the general part of the present chapter (excepting the butyro-refractometer reading, for which *see* Butter, Vol. II).

(*c*) Elaidin test (*see* General Methods, 24).

(*d*) The arachidic and lignoceric acid test and the Tortelli and Fortini tests for erucic acid (*see* Arachis Oil and Colza Oil).

(*e*) The colour reactions of Heydenreich, Hauchecorne, Brullé, Bellier, Milliau, Halphen, and Villavecchia and Fabris (*see* General Methods, 23 ; also Cottonseed Oil and Sesamé Oil).

(*f*) With industrial olive oils, determinations of the moisture and extraneous impurities are necessary (*see* General Methods, 1), and it is sometimes required to ascertain if the oil has been extracted with carbon disulphide (*see* later, 8).

**2. Detection of Extraneous Oils.**—The various foreign oils which may be mixed with olive oil are detected as follows :

1. Arachis Oil : by the presence of arachidic and lignoceric acids, the quantity of which gives an approximate measure of the amount of the oil (*see* Arachis Oil).

2. Colza or Ravison Oil : by the Tortelli and Fortini test (*see* Colza Oil). In considerable proportion it lowers the melting and solidifying points

of the fatty acids and the saponification number and raises the Maumené number and refractometric value of olive oil.

3. COTTONSEED OIL: by the reactions of Halphen and Milliau (modified by Armani and by Tortelli and Ruggeri) (*see* Cottonseed Oil). Further it raises the specific gravity, the melting and solidifying points of the fatty acids, the Maumené number, the refractometric value and the iodine number.

4. SESAMÉ OIL: by the Villavecchia and Fabris reaction (*see* Sesamé Oil); it alters the different characters in the same sense as does cottonseed oil.

5. OTHER SEED OILS IN GENERAL: by the general colour reactions already indicated (*see e*, above) and by certain alterations in the characters of the oil.

6. ANIMAL OILS: by the smell and by testing for cholesterol as indicated for tallow (olive oil scarcely contains traces of phytosterol). Fish oils and oils of other marine animals are detected by the Tortelli and Jaffe reaction (*see* Fish Oils).

7. MINERAL OILS: by the lowering of the saponification number and by examination of the unsaponifiable part (*see* General Methods, 19).

**3. Detection of Sulphocarbon Oil.**—200 grams of the oil are vigorously shaken with 50 c.c. of 90% alcohol and distilled from a water-bath, the distillate being collected in a flask containing a few c.c. of alcoholic caustic potash solution (1 : 10) (recently prepared from the purest alcohol) and immersed in cold water. When about two-thirds of the alcohol added to the oil are collected, the distillation is interrupted. The distillate is faintly acidified with dilute acetic acid and treated with 1–2 drops of dilute copper sulphate solution: in presence of potassium xanthate (formed by the action of the carbon disulphide, distilled with alcohol, on the alcoholic potash), a brown coloration is formed and then a yellow precipitate of copper xanthate.[1] The presence of carbon disulphide in the oil is hence concluded.

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Genuine *comestible olive oil* should have the following characters:

It should be clear and have the normal odour and taste.

*Solidifying point*: it should begin to become turbid at about 10°, and as a rule it sets to a semi-solid mass between 6° and 2°; at 0° it forms a soft solid.

*Melting point of the fatty acids*: 22–28°.

*Solidifying point of the fatty acids*: 24–21°.

*Specific gravity* at 15°: 0·914–0·919.

*Reading on Zeiss butyro-refractometer* at 25°: 62–63. With oils which are defective or altered, or obtained from bad olives, or washed or extracted with carbon disulphide, the reading may be as low as 60.

*Maumené number* (Tortelli): 41–47° (44° may be taken as the mean). With the Jean thermo-oleometer: 32–39°.

*Acid number*: 2 at the most.

*Saponification number*: 185–196 (normally 192–195).

*Iodine number*: 79–88. Most commonly the iodine number is 80–83, only certain oils from Liguria and Spain, and more often the oils of Crete, Tunis,

[1] Well refined sulphocarbon oils and those heated for an hour at 130° no longer give the above reaction or any other reaction specific for carbon disulphide or other sulphur compound.

Morocco and India, have a higher number (85–88). With some Moroccan oils a number of 90 or more is obtained, but such cases are exceptional and sometimes relate to oils not of the olive but of the fruits of the Moroccan olive (*Arganum sideroxylon*), a tree of that region very similar to the olive.[1]

*Elaidin test*: should give a colourless or yellowish solid mass.

*Fatty acid test*, according to Tortelli and Fortini: negative result.

*Colour reactions*: none should be given, either with the general reagents for seed oils or with the special reagents for cottonseed, sesamé and marine animal oils.

In general, an olive oil may be regarded as pure when: it is coloured only pale yellow by Heydenreich's, Hauchecorne's or Brullé's reagent, has a saponification number not less than 192 and an iodine number not exceeding 83, and does not contain arachidic, lignoceric or erucic acid. An oil with a saponification number less than 192 and an iodine number above 83—within, however, the limits indicated in Table XLIV—but of normal behaviour as regards all the other tests, may be regarded as genuine.

The official Italian methods give for olive oil the limits indicated above for the different characters, excepting that the solidifying temperature is given as 2–6°, the refractometer reading at 25° as between 62 and 62·8, and the iodine number as 79–90. They give further: Reichert-Meissl number, 0·3; Hehner number, 95·5–96·2; acetyl number, 4–10; absolute iodine number, 95–104; unsaponifiable residue, which should be constituted of minimum traces of phytosterol scarcely sufficient for the reaction with chloroform and sulphuric acid (100 grams of the oil yield 0·45–0·47 gram of crude phytosterol, whilst sesamé and cottonseed oils give respectively 1·28 and 1·20 gram).

The *industrial oil for lighting or lubrication* should answer the requirements indicated for the genuine comestible oil. In some cases, however, admixtures of seed oils (arachis, colza or ravison) are allowed, e.g., by the Italian State Railways. It should not contain more than 1% of free acid (expressed as monohydrated sulphuric acid), should not congeal above — 5°, should not be adulterated with animal, mineral or resin oils, and should not contain mucilaginous substances or suspended foreign matters. Further, that for illuminating purposes should satisfy definite requirements with regard to the mode of burning, the illuminating power, etc.

*Industrial olive oil for soap-making* occurs in various qualities:

*Washed oil*, obtained by washing the olive residues (sanse): moisture and impurities up to 2%; free from sulphur; acidity variable (10–40% as oleic acid).

*Huile lampante* (yellow and green), obtained by filtering the washed oil: moisture and impurities up to 1%.

*Olive oil grease* or residues from the filtration of the washed oil: should be free from sulphur, unbleached and not treated with acid. Its value depends on its content in total fatty matter—to be determined directly—or on its content in fatty acids (exclusive of hydroxy-acids)—to be determined by saponifying the grease and separating the total fatty acids.

*Sulphur or sulphocarbon olive oil*, which is distinguished from sanse oil: saponification number not less than 180, acidity (as oleic acid) up to 65%, moisture and impurities up to 2% and hydroxy-acids up to 3%.

## CASTOR OIL

From the seeds of *Ricinus communis*, is almost colourless or yellowish, dense and viscous, with characteristic smell and taste. It dissolves in alcohol in all proportions and in acetic acid in the cold. It is, however, almost insoluble in petroleum ether and in vaseline oil, whilst other oils are

[1] *Zeitschr. Unt. Nahr. Genussmittel*, 1910, II, p. 749.

soluble in these solvents. Its physical and chemical characters are given in Table XLIV.

Castor oil is readily distinguished from other oils by its solubility in alcohol and its insolubility in mineral oils, by its specific gravity, acetyl number, viscosity and rotatory power, which are considerably higher than with other oils. Its viscosity (Engler) at 50° is about 16 (water at 20 = 1) and its rotation in a 20 cm. tube at the ordinary temperature + 8° to + 9° (circular degrees).

When prepared recently and in the cold, it is neutral, but it easily becomes rancid. Old oils and those extracted in the hot or by solvents are more or less acid (up to more than 20% of free acids, as oleic acid).

The following tests are usually made:

**1. Solubility.**—This serves to show if the oil is pure or not, and is carried out as follows:

(a) *Finkener's test.* 10 c.c. of the oil and 50 c.c. of 90% alcohol are shaken together: if the mixture is turbid and remains so at 20°, the castor oil is not pure.

(b) *Morpurgo's test.* 1 vol. of the oil and 3 vols. of oil of vaseline are shaken together at 10–15°: after standing, the oil of vaseline separates with its original volume if the castor oil is pure, but with an increased volume if extraneous oils are present.

**2. Detection of Adulterations.**—(*a*) VARIOUS VEGETABLE OILS. Castor oil is rarely adulterated with vegetable oils (cottonseed, sesamé, colza, linseed, etc.), which may in any case be easily detected, since they lower the specific gravity, acetyl number and rotatory power and raise the saponification number (excepting colza or ravison oil).

(*b*) CROTON ELLIOTIANUS OIL. This oil does not greatly alter the properties and is difficult to detect, especially if only in small proportion. An indication of its presence may, however, be obtained by boiling the oil with a very concentrated potassium hydroxide solution: on cooling, a white, soapy mass is obtained with pure castor oil, and a yellow or brown mass in presence of croton oil (1% or more).[1]

**3. Test for Resinous Substances.**—To ascertain if a sample of castor oil is contaminated with resinous substances or has been *extracted in the hot*, the following test, prescribed by the official Italian pharmacopœia, is made. 3 c.c. of the oil, 3 c.c. of carbon disulphide and 1 c.c. of conc. sulphuric acid are shaken together for some minutes: the mixture should not turn brown.

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*Medicinal castor oil*, according to the official Italian pharmacopœia, should be extracted by pressure in the cold from husked, peeled seeds; it should be clear, almost colourless or yellowish, and not of acrid taste, soluble in 5 parts of 90% alcohol at 15° and in 2 parts at 25°, and extremely soluble in absolute alcohol, ether or glacial acetic acid. Its iodine number should be 80–85, and its saponification number 180–182, and it should answer to the reaction, described

[1] Mazzucchelli: Detection of croton oil in castor oil (*Arch. di farm. sper.*, 1905, p. 223).

## TABLE XLIV

## Characters of Vegetable Oils[1]

| | Specific Gravity at 15°. | Solidifying Point. | Zeiss Butyro-refractometer Reading. t. | | Maumené Number (J = Jean, T = Tortelli apparatus). | Saponification Number. | Iodine Number. | Fixed Acid Number. | Volatile Acid Number. | Fatty Acids. Melting Point. | Solidifying Point. | Acetyl Number. | Iodine Number of the Liquid Acids. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Almond | 0·914–0·920 | −10 to −15° | 25° | 64–65 | 50–51 T | 187–196 (192 | 93–103 (95) | 96–97 | — | 12–15° | 5–11° | 5–6 | 102 |
| Apricot kernel | 0·915–0·921 | −14 to −20 | 25 | 65–67 | 60–61 T | 187–193 | 96–109 (100) | 95–96 | — | 2–7 | 0–4 | — | 111–112 |
| Arachis | 0·916–0·920 | −3 to −7 | 25 | 62–67 | 51–60 T | 185–197 (193) | 83–103 (92–95) | 95–96 | 1 | 27–33 | 22–32 | 3–4 | 105–128 |
| Baobab seeds (Andansonia) | 0·915–0·919 | +3 to −3 | — | — | — | 190–192 | 76–79 | — | — | 35–38 | 32–34 | — | 97–98 |
| Beechnut | 0·920–0·922 | −17 | — | — | 63–65 J | 191–196 | 104–111 | 95 | — | 23–24 | 17 | — | — |
| Ben (*Moringa pterigosperma Gaertn.*) | 0·912–0·919 | 0 | ? | 50–60 | — | 185–188 | 72–112 (80–84) | 95 | 0·5 | — | 37–38 | — | — |
| Brazil nut (*Bertholletia excelsa H.B.*) | 0·917–0·919 | 0 to −4 | — | — | 50–52 J | 170–194 | 90–106 | — | — | 28–30 | 25–27 | — | — |
| Cameline (German sesamé oil) | 0·920–0·933 | −18 | — | — | 103 T | 188 | 132–153 (150) | — | — | 18–20 | 13–14 | — | 165–166 |
| Candle nut (Kekuna) (*Aleurites moluccana, A. triloba Wild*) | 0·920–0·926 | −18 to −20 | ? | 76 | — | 179–195 | 136–164 | 90 | 1–3 | 18–21 | 13–15 | 9–10 | 186 |
| Cashew nut | 0·916 | — | 25 | 62 | — | 179–195 | 60–84 | — | — | — | — | — | — |
| Castor | 0·960–0·973 | −10 to −18 | 25 | 78 | 74 T | 176–186 (180) | 82–91 (85) | — | 2–3 | 13 | 2–3 | 146–156 | 106–107 |
| Colza and Ravison | 0·913–0·918 | −3 to −10 | 25 | 68–71 | 61–62 T | 167–180 (177) | 94–106 (100) | 95–96 | 0·5 | 17–24 | 12–18 | 6 | 114–126 |
| Cottonseed | 0·922–0·931 | +12 to −12 | 25 | 67–70 | 78 T | 190–198 (193–195) | 101–117 (108) | 95–96 | — | 34–40 (34–37) | 32–35 | 15–17 | 146–152 (148) |
| Croton Elliotianus | 0·942–0·944 | −16° | 40 | 68 | — | 210–215 | 101–109 | 89 | 12–14 | 16–19 | 14–18 | 8–9 | — |
| Curcas | 0·911–0·924 | 0 to −8 | — | — | 68–69 T | 193–210 | 98–110 | 88–95 | 1 | 24–30 | 20–26 | 9 | — |
| Fir seed | 0·928–0·933 | −27 | — | — | 98–99 J | 191–193 | 120–121 | 91–92 | — | 16–19 | 10–15 | — | — |
| Grape seed | 0·935–0·956 | −13 to −17 | 25 | 68–71 | 64–74 T | 178–190 | 94–143 | 92–98 | 0·5 | 23·26 | 18–20 | 31–44 | 151–152 |
| Hazelnut | 0·914–0·924 | −20 | 25 | 61–62 | 45–48 T | 187–192 | 83–90 | 95–96 | 1 | 17–25 | 15–20 | 3 | 97–99 |
| Hempseed | 0·925–0·931 | −15 to −27 | — | — | 95–99 J | 190–195 | 140–166 (150) | — | — | 17–19 | 14–16 | 7–8 | — |
| Indian laurel | 0·926 | −15 | — | — | — | 170–190 | 86–119 | — | — | 24–26 | 16–19 | — | — |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Jamba | 0·915–0·916 | −12 | — | — | 51–53 J | 172 | 95–96 | 96–97 | — | 19–21 | 11–16 | — | — |
| (*Brassica campestris L., var.*) | | | | | | | | | | | | | |
| Japan (Chinese) wood | 0·933–0·944 | −17 to −20 | — | — | — | 190–197 | 150–176 | 96–97 | — | 30–40 | 27–37 | — | 145? |
| (*Aleurites cordata Müll.*) | | | | | | | | | | | | | |
| Kapok | 0·923–0·933 | −10 | 25 | 64–68 | 95 J | 189–195 | 73–96 | 95 | 3–4 | 27–38 | 22–34 | 86 | — |
| Lentisk | 0·925 | 0 | — | — | — | 182 | 92 | — | — | 32–35 | 27–30 | — | — |
| Linseed | 0·930–0·937 | −16 to −27 | 25 | 81–87 | 124–138 T | 187–195 (192) | 164–194 (170–190) | 95–96 | — | 17–24 | 13–20 | 8–9 | 190–210 |
| Madia | 0·926–0·935 | −10 to −20 | — | — | 96–101 J | 192–193 | 117–120 | — | — | 23–26 | 20–22 | — | — |
| Maize (corn) | 0·921–0·926 | −10 to −20 | 25 | 71–72 | 82 T | 188–198 (190) | 111–128 (120) | 92–95 | 0·3–4 | 18–23 | 14–16 | 11–12 | 140–144 |
| Moroccan olive | 0·918–0·919 | — | — | — | — | 192 | 94–96 | — | 1–2 | — | — | — | — |
| (*Argania sideroxylon*) | | | | | | | | | | | | | |
| Mustard seed, black | 0·915–0·920 | −17 | 25 | 69 | 74–77 T | 174–182 | 96–122 | 95–97 | — | 16–17 | 15 | — | — |
| Mustard (Hedge) | 0·917 | −8 | — | — | — | 174 | 105 | — | — | 12–13 | — | — | — |
| Do. Indian | 0·916–0·920 | — | 40 | 60 | — | 172–180 | 102–108 | 95–96 | 0·3–1 | — | — | — | — |
| Do. White | 0·913–0·920 | 16 | 40 | 85–86 | 58–59 T | 170–176 | 92–103 | 96 | — | 15–16 | 12–14 | — | — |
| Niger seed (Guizotia) | 0·923–0·928 | −7 to −13 | 40 | 63 | 91–96 T | 189–192 | 126–134 | 94 | 0·5 | 29–33 | 28–30 | — | 147–148 |
| Olive | 0·913–0·919 (0·916–0·918) | 0 to 6 | 25 | 62–63 | 41–47 T (44) | 185–196 (192–195) | 79–88 (80–83) | 95–96 | 0·3 | 22–28 | 21–24 | 4–10 | 95–104 |
| Peach kernel | 0·918–0·923 | −20 to −23 | 25 | 63–67 | 51–53 T | 189–192 | 94–96 | — | — | 5–14 | 4–7 | 6–7 | 102–104 |
| Perilla | 0·930 | — | — | — | — | 189–190 | 206 | — | — | 5 | — | — | — |
| Pistachio nut | 0·918 | −10 to −11 | 25 | 62 | 55 T | 191–192 | 86–93 | 96 | — | 17–20 | 13–14 | — | 105–106 |
| Plum kernel | 0·912–0·919 | −5 to −10 | 25 | 63–64 | 44–45 T | 189–192 | 91–101 | 96 | — | 11–21 | 7–15 | — | — |
| Poppyseed | 0·924–0·937 | −18 | 25 | 71–74 | 88–89 T | 190–198 (193) | 131–157 (137) | 94–96 | 0 | 20–21 | 15–17 | 13 | 149–150 |
| Radish | 0·914–0·918 | −15 | 40 | 57–58 | 51–52 J | 173–179 | 93–112 | 96 | 0·3 | 20 | 13–15 | — | — |
| Rice (germ) | 0·907–0·923 | −10 | 25 | 68–69 | 67 T | 181–198 | 91–108 | 95–96 | 1 | 31–36 | 28–29 | — | 130–131 |
| Rubber seed | 0·922–0·930 | −21 | — | — | — | 191–206 | 117–141 | 95 | 0–3 | — | 15 | 28 | 155 |
| Safflower | 0·928–0·938 | −13 to −20 | 25 | 77–78 | 101–120 T | 186–195 | 126–150 (140) | 91–95 | 1–2 | 11–17 | 7–12 | 53 | 140–151 |
| Sesamé | 0·922–0·926 | −5 | 25 | 66–70 | 71 T | 187–193 (190–192) | 102–116 (108) | 95–96 | 1 | 25–35 (27–30) | 23–32 (23–25) | 11–12 | 129–140 |
| Soya bean | 0·924–0·929 | −10 to −15 | 25 | 73–74 | 83 T | 182–193 (185) | 115–137 (133–135) | 94–96 | 0·1 | 20–29 (24–25) | 16–25 (20–21) | — | 143–144 |
| Stillingia | 0·939–0·943 | below 0 | 25 | 86 | 136–138 | 204–210 | 145–161 | 94–96 | 1 | 14–15 | 12–13 | 28–29 | 178 |
| Sunflower | 0·923–0·936 | −16 to −18 | 25 | 72–73 | 88 T | 188–194 | 120–137 (133) | 95 | — | 17–24 | 17–18 | — | 154 |
| Tomato seed | 0·920–0·924 | −20 | 25 | 71–72 | — | 183–191 | 106–118 | 95–96 | 2 | 26–29 | — | — | 130–142 |
| Walnut | 0·925–0·926 | −15 to −27 | 40 | 65–68 | 104 T | 188–197 (194) | 143–152 (148) | 95–96 | 0 | 16–20 | 13–16 | 7–8 | 166–167 |
| Wheat (germ) | 0·924–0·929 | −15 | — | — | — | 182–190 | 115–123 | — | — | 39–40 | 29–30 | — | — |

[1] The numbers in brackets indicate the more common limits or mean values.

above, with carbon disulphide and sulphuric acid. Freshly prepared and dissolved in alcohol, it should have no acid reaction.

*Castor oil for industrial purposes* (soap-making) may have: moisture and impurities up to 1%; D = 0·960–0·974; iodine number, 82–86; solidifying point, — 10° to — 18°; solidifying point of the fatty acids = 3°; acetyl number of the fatty acids = 153·4–156; Maumené number (Tortelli) = 67·8°.

## SESAMÉ OIL

From the seeds of *Sesamum indicum* and *S. orientale*, is more or less deep yellow, of faint special odour and pleasant taste. From 16 to 19 grams dissolve in 1000 c.c. of absolute alcohol at 15°. Its characters are given in Table XLIV.

With Heydenreich's, Hauchecorne's, Brullé's and Bellier's reagents it gives the colorations usual for seed oils. Characteristic of sesamé oil is the following colour reaction, which serves to detect it in olive oil and in all other oils and fats.

**1. Villavecchia and Fabris Reaction.**[1]—Two or three drops of alcoholic furfural solution (2 grams of furfural in 100 c.c. of 95% alcohol)[2] and then 5–10 c.c. of the oil and 10 c.c. of pure conc. hydrochloric acid (D 1·19) are poured into a test-tube, the whole being well shaken for a few moments and then left to stand. The acid, coloured dark red, soon separates in the lower part of the tube and becomes increasingly dark, while the upper oily layer represents a yellowish-red emulsion. The coloration is clearly observable even with mixtures containing only 0·5% of sesamé oil.

No other oil gives such a reaction; only certain olive oils (from Tunis and Algeria, and some from Bari, Brindisi and Lecce) may yield with the above reagent a pink or reddish colour, which is, however, always less intense than and *quite different* in tint from that produced by sesamé oil. In doubtful cases, the reaction may be carried out with the liquid fatty acids separated by Tortelli and Ruggeri's method (*see* General Methods, 18, 1).

**2. Detection of Adulterations.**—Sesamé oil may be adulterated with drying oils, colza oil and arachis oil: the first raise the iodine number and the Maumené number, while the others are detectable by testing for the arachidic and lignoceric acids and by the Tortelli and Fortini test (*see* Arachis Oil and Colza Oil).

***

*Comestible sesamé oil* should be clear, of normal taste and odour, and not too acid (fresh oil may contain 0·5–5% of free acids, calculated as oleic acid; old oils may contain as much as 35%).

The permissible limits for the *industrial oil* (for soap-making) are: moisture

[1] This reaction (see *Zeitschr. für angew. Chemie*, 1892, p. 509, and 1893, p. 505) is due to the action of furfural, in presence of conc. hydrochloric acid, on the methylene ether of hydroxyhydroquin onecontained in sesamé oil, according to the investigations of Malagnini and Armani (see *Rend. Soc. chim. di Roma*, 1907, V, p. 133). It serves as a rational substitute for *Baudouin's reaction*, which consisted in shaking the oil with conc. hydrochloric acid and sugar. In Baudouin's reagent also the active principle is furfural, which is formed by the action of the acid on the saccharose, but, this formation being slow and limited, Baudouin's reaction is less rapid and certain.

[2] The furfural should be pure and recently distilled, so that it shows little colour.

and impurities, up to 1%; D = 0·920–0·924; iodine number = 100–114; Maumené number (Tortelli) = 71·3°; solidifying point of the fatty acids = 18–23·4°.

## Vegetable Fats

These are fatty substances of vegetable origin and solid at the ordinary temperature. Among them are also some so-called *Vegetable waxes*, such as Japan wax and myrtle wax, which are, however, not true waxes but solid fats, since they are composed of glyceryl esters and not esters of higher alcohols.[1] True waxes of vegetable origin include only carnauba wax and a few others (*see* Waxes).

The more important vegetable fats are those of cacao, coco-nut, palm and palm-kernel, vegetable tallow and a few others which are described; their characters are given in Table XLV, together with those of other vegetable fats of some interest.

### CACAO BUTTER

### (Cocoa Butter)

From the seeds of *Theobroma cacao*, is a somewhat brittle, yellowish-white solid with a taste and smell recalling those of torrefied cacao. It dissolves in 5 parts of boiling absolute alcohol and is almost insoluble in 90% alcohol; it is soluble in 3 parts of ether. It does not readily turn rancid, and only when very old or badly stored does it contain more than 1% of free acid (calculated as oleic acid); the rancid fat is white. Fat from the skins of cacao seeds is, however, markedly acid even when fresh. The characters of the fat are given in Table XLV.

**Detection of Adulterations.**—It may be adulterated with coco-nut butter, tallow, stearine, solid paraffin and wax, or, more rarely, with other vegetable fats (Japan wax, Dika oil), almond oil, hazelnut oil or other seed oils. Such adulterations are detected by determining the different characters of the fat, bearing in mind the following:

Coco-nut oil raises the saponification number and the volatile acid number, but lowers the iodine number and the refractometric reading. Stearine raises the acid number and lowers the iodine number, and is, moreover, easily detectable by its ready solubility in alcohol. Solid paraffin and wax lower the saponification number and the iodine number and may be recognised in the unsaponifiable portion. Vegetable oils in general lower the specific gravity and the melting point and raise the iodine number and the refractometric reading. Japan wax increases the density, the acid number and the saponification number and lowers the iodine number. Dika oil raises the saponification number and the refractometric value and lowers the iodine number (*see* Table XLV). Tallow is not easily detectable by physical and chemical characters alone, but its presence may be shown by the cholesterol test (*see* Lard).

[1] These vegetable waxes are distinguishable from true waxes in that they are completely saponified by alcoholic potash, yielding soaps entirely soluble in water.

## Table XLV

## Characters of Vegetable Fats [1]

| | Specific Gravity. t. | | Melting Point. | Solidifying Point. | Zeiss Butyro-refractometer Reading. t. | | Saponification Number. | Iodine Number. | Fixed Acid Number. | Volatile Acid Number. | Fatty Acids. Melting Point. | Solidifying Point. | Acetyl Number. | Iodine Number of Liquid Acids. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Borneo tallow (Tangkawang fat) (*Shorea and Dipterocarpus spec.*) | 100° | 0·854–0·856 | 34–43° | 22–27° | 40° | 45–46 | 191–196 | 29–30 | 95–96 | — | 54–55° | 48–54° | — | — |
| Cacao butter . . . . . | 15 | 0·940–0·976 (0·950) | 26–36 (30–35) | 20–27 | 40 | 46–48 | 192–204 (195) | 28–42 (35–40) | 94–95 | 1–4 | 48–53 | 45–51 | 3 | — |
| | 100 | 0·857–0·858 | | | | | | | | | | | | |
| Carapa oil (African) (Touloucoona oil) . . . . . (*Carapa guineensis Sweet*) | 15 | 0·912–0·923 | 23–31 | 18–26 | — | — | 195–196 | 65–72 | 93–94 | 4–5 | 36 | 32–33 | — | — |
| Carapa oil (Guiana) (Andiroba oil) . . . . . (*Carapa guianensis Aubl.*)[2] | — | — | liquid | — | — | — | — | — | — | — | — | 36 | — | — |
| Carapa grandiflora oil . . . | 40 | 0·917–0·921 | 15–20 | 8–10 | — | — | 198–202 | 72–84 | — | 3–4 | — | 35–39 | — | — |
| Coco-nut oil . . . . . | 15 | 0·925 | 20–28 | 14–26 | 40 | 33–36 | 246–268 (260) | 8–10 | 83–92 | 7–9 | 21–27 | 16–20 | — | 54 |
| | 100 | 0·863–0·874 | | | | | | | | | | | | |
| Dika oil (Wild mango or oba oil) (*Irvingia Barteri Hook*) | 15 | 0·910 | 30–42 | 27–35 | — | — | 244–245 | 5 | — | 0·4 | — | 3–5 | — | — |
| | 100 | 0·820 | | | | | | | | | | | | |
| Fulwah butter (Indian butter) (*Bassia butyracea Roxb.*) | 15 | 0·955 | 30–49 | 27–45 | 40 | 57–60 | 175–191 | 42–51 | 94–96 | 0·4–3 | 58–59 | 56–57 | — | — |
| | 100 | 0·897 | | | | | | | | | | | | |
| Hydnocarpus oil (Chaulmoogra, Krebao or Lukrabo oil)[3] . (*Taraktogenos Kurtii King and Hidnocarpus anthelmintica Pier.*) | 25 | 0·951–0·958 | 22–26 | 14–19 | — | — | 205–232 | 86–103 | 95–96 | — | 44–45 | 41–42 | — | — |
| Illipé butter (Mahua butter) . (*Bassia latifolia Roxb.*) | 15 | 0·917 | 25–40 | 20–36 | 40 | 51–55 | 187–200 (190) | 50–68 (60) | 94–95 | 1 | 39–45 | 38–40 | — | — |
| | 100 | 0·894–0·898 | | | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Japan wax (*Rhus succedanea L., R. Vernicifera D. C., etc.*) | 15<br>100 | 0·970–1·000<br>0·873–0·875 | 48–55 | 45–53 | 40 | 47 | 206–238<br>(220) | 4–13<br>(9) | 90–91 | — | 56–57 | 53–56 | 27–31 | — |
| Laurel butter, from the fruit (*Laurus nobilis L.*) | 15 | 0·933–0·953 | 32–36 | 24–25 | 40 | 72 | 197–199 | 68–96 | 83 | 3–5 | 23–24 | 14–19 | — | 98 |
| Mafura tallow (*Trichilia emetica, T. subcord. Vahl*) | 100 | 0·857 | 35–45 | 25–37 | — | — | 198–221 | 40–47 | 93 | 1–4 | 51–55 | 44–52 | — | — |
| Mohwah butter (Bassia tallow)[4] (*Bassia longifolia Roxb.*) | 15<br>100 | 0·917<br>0·897–0·898 | 25–42 | 20–36 | 40 | 52 | 190–200 | 60–68 | 94–95 | 1–2 | 39–45 | 38–41 | — | — |
| Myrtle wax | 15<br>100 | 0·995–1·000<br>0·875–0·878 | 40–48 | 39–45 | 40 | 55 | 205–217 | 10–11 | — | — | 47–48 | 46 | — | — |
| Njave butter (Djave butter) (*Bassia Djave D. Lan.*) | 40 | 0·898 | 44–47 | 38–40 | 40 | 52 | 182–190 | 56–59 | 94–96 | 1–3 | 46–51 | 43–47 | 13 | — |
| Nutmeg butter (mace butter) (*Myristica fragrans Hoult*) | 15<br>100 | 0·945–0·996<br>0·884–0·898 | 25–51<br>(25–30) | 24–44 | 40 | 48–85 | 154–191 | 31–81 | — | 1–4 | 40–49 | 39–45 | — | 93–94 |
| Palm | 15<br>100 | 0·945–0·947<br>0·858–0·860 | 30–43 | 26–40 | 40 | 47 | 195–207 | 34–58 | 95–98 | 1 | 44–50 | 40–49 | 18 | 95 |
| Palm kernel oil | 15<br>100 | 0·952–0·955<br>0·867–0·873 | 23–30 | 20–27 | 40 | 36–37 | 241–260 | 10–20 | 87–92 | 4–7 | 20–28 | 20–25 | 2–9 | — |
| Shea butter (Galam or Karité butter) (*Bassia Parkii D. C.*) | 15<br>100 | 0·953–0·955<br>0·859–0·896 | 23–31 | 17–27 | — | — | 177–187 | 49–67 | 94–95 | 1–2 | 39–56 | 38–54 | — | — |
| Stillingia ("Prima" vegetable tallow, Pi-ieou, Pi-yu) | — | — | 47–52 | 45–50 | 50 | 38 | 205–231 | 16–19 | — | — | 55–57 | 53–54 | — | — |
| Stillingia ("Secunda" vegetable tallow, Mou-ieou) | 15<br>100 | 0·918–0·922<br>0·860 | 36–47 | 27–34 | 40 | 44–45 | 196–207 | 28–100<br>(30–45) | 95–96 | 1 | 53–57 | 52–55 | — | — |
| Ucuba wax (Ocuba wax) | 20 | 0·912 | 39–43 | 32–33 | — | — | 219–220 | 9–10 | 93–94 | — | 42–46 | — | — | — |
| Vateria (Malabar or Piney) tallow | 15<br>100 | 0·915<br>0·890 | 36–42 | 30–40 | 40 | 42–47 | 188–192 | 30–45 | 95 | 0·3 | 56–57 | 54–55 | — | — |
| Virola tallow | 50 | 0·896–0·900 | 41–47 | 38–45 | — | — | 221–244 | 12–14 | — | — | 38–43 | 36–39 | — | — |

[1] The numbers in brackets indicate the more usual limits or mean values. [2] Dextro-rotatory. [3] Dextro-rotatory: $[\alpha]_D$ = 52–57°. [4] Dextro-rotatory: $[\alpha]_D$ = about 1.

For testing for extraneous fats in general, recourse may also be had to determinations of the critical solubility temperature in absolute alcohol and in glacial acetic acid and of the melting points of glycerides insoluble in a mixture of alcohol and ether, as suggested by Grimm.[1]

***

Cacao butter is to be regarded as genuine when its physical and chemical characters lie within the limits indicated in Table XLV and it does not contain any of the above-mentioned impurities.

It should be noted that *substitutes for cacao butter* are sold under various names, e.g., *chocolate butter*, consisting of coco-nut oil; *cacao butter* (coco-nut oil and Japan wax). The so-called *Samana cacao butter* is a fat which melts at about 12° and when left for a long time separates a liquid part; it has D at 17·5° = 0·906, refractometric reading at 40° = 50·5 and iodine number = 53–59.

## COCO-NUT OIL

From the albumin or pulp of the coco-nut, fruit of *Cocos nucifera*. It is white or pale yellow, and has the consistency of butter and a special odour. In coco-nut butter well refined for comestible use this odour is almost entirely lacking, but boiling with a little alcohol and a few drops of conc. sulphuric acid brings out the odour distinctly.

It dissolves in 2 vols. of absolute alcohol at 30° and in 2 vols. of 90% alcohol at 60°. Its physical and chemical characters are given in Table XLV.

With Heydenreich's, Hauchecorne's or Brullé's reagent it gives no sensible coloration, and it does not react with silver nitrate or with furfural and hydrochloric acid. Characteristic of coco-nut oil are the rather high saponification number, the low iodine number and the volatile acid number, which is greater than those of vegetable oils and fats in general.

***

*Pure, edible coco-nut oil* is perfectly white (sometimes dyed yellowish to imitate butter), odourless and neutral or almost so (acidity number not beyond 1% as oleic acid) and has a fresh, pleasant taste.

*Industrial coco-nut oil* (for soap) is white or faintly yellow and has a more or less pronounced taste and smell. The finest and whitest quality bears the name *Cochin neige*, while the others are called *White Cochin, Ceylon* and *Copra oils*.

The allowable limits for these industrial oils are: acidity (as oleic acid) up to 4% for Cochin and up to 10% for other qualities; moisture and foreign impurities, up to 1%; m.pt. = 20–28°, setting point = 22–14°; titer (setting point of the fatty acids) = 16–23°; volatile acid number = 5·6–8·5; saponification number = 248–260; iodine number = 7·68–9·5.

## PALM OIL

From the flesh of the fruit of the oil-palm (*Elaeis guineensis* and *E. melanococca*). It has the consistency of butter, a more or less intense yellow or orange colour which weakens considerably on exposure to air and light, and a pleasant smell recalling that of the iris.

[1] *Chem. Rev. Fett.-Ind.*, 1914, pp. 47 and 74.

With chloroform and sulphuric acid it gives a reaction similar to that of cholesterol (*see* General Methods, 19).

Its value depends essentially on the content of moisture and foreign impurities and on the setting point of the fatty acids (titer). These, then, are the principal determinations made (*see* General Methods, 1, and also Tallow); the acid saponification number is also measured and sometimes the glycerine content (*see* General Methods).

***

The titer of palm oil generally lies between 40° and 50°. Its content of water and foreign matters varies from 0·5% to 17%, but with a good specimen should not exceed 2%. Commercial palm oil is always markedly acid; when recently prepared the oil may contain about 10% of free acids (calculated as palmitic acid), but most commercial oils show 20–50%, while certain old oils of special type may contain nearly 90%. As a rule the content of glycerine diminishes as the free acid increases.

The best commercial oil is that from *Lagos*, with 2% of moisture and impurities at most; minimum titer, 43°; acidity usually not greater than 20%; saponification number, 196–207. The *Benin* oil, which is brown, has the titer 40–49° and acidity up to 50%.

## PALM-KERNEL OIL

From the seeds of the oil-palm (*Elaeis guineensis* and *E. melanococca*). It has the consistency of butter, is white or yellowish, has a special odour similar to that of coco-nut oil and readily becomes rancid. In all its properties it closely resembles coco-nut oil (*see* Table XLV), from which it is difficult to distinguish it. Analysis of this oil is carried out like that of coco-nut oil (*q.v.*).

***

In palm-kernel oil for industrial purposes up to 1% of moisture and extraneous impurities are allowed and up to 10% of free acids; saponification number = 241–250; volatile acid number = 4·8–5·6; titer = 20·5–25·5°.

## OTHER VEGETABLE FATS

Of the other vegetable fats the following are commonly known and used:

**Vegetable Tallow or Chinese Tallow** (*Stillingia fat*), from the seeds of *Stillingia sebifera*. Its characters and properties may vary with the method of extraction, but it is usually solid, hard and white outside and more or less stained with earthy and vegetable residues, yellowish inside, and odourless, or almost so.

**Illipé-nut Butter, Fat or Oil** (*Mahwa fat*), from the seeds of *Bassia latifolia*. It has a tallowy consistency, a yellowish or greenish colour and a slight aromatic odour, and readily turns rancid.

**Mowrah Butter, Fat or Oil,** from the seeds of *Bassia longifolia*; of tallowy consistency, yellowish colour when fresh, rather bitter taste, and odour recalling that of cacao seeds; it easily becomes rancid and decolorised.

The analysis of these, as of any other vegetable fat, comprises determinations of moisture and foreign impurities, titer, acidity and saponifica-

tion numbers, and any other characters which may serve to establish its origin (*see* Table XLV).

## Animal Fats

The most important animal fats are: butter, dealt with in the chapter on milk and its products (*see* Vol. II, Chapter II), tallow, lard, bone-fat and the foot-oils, which are considered below in detail; a large number of other fats are obtained from different animals, but few are of importance. The characters of these are given in Table XLVII.

So-called *wool fat*, which from its composition is to be regarded as a wax, is dealt with in the article on waxes.

### TALLOW

This is a fat obtained from bovine (ox-tallow) and from ovine animals (sheep's or goat's fat). It is stiff and yellowish and has a characteristic smell; in the light and air it rapidly becomes rancid and decolorised. One part of it dissolves in 40 parts of 94% alcohol. Its physical and chemical characters are given in Table XLVII.

Its analysis includes firstly the determination of the titer (solidifying point of the fatty acids), on which depends the commercial value (*see* 1). Determinations are also to be made of the water and foreign impurities, of the acid and saponification numbers and, sometimes, of the glycerine (*see* General Methods). Any adulteration with bone fat, wool fat, palm oil or coco-nut oil, may be detected as described below (2).

**1. Titer Test.**—The sample for this determination must be taken carefully, portions being taken from each cake or cask (at different points) of the bulk and these melted together at a temperature not exceeding 60° and the fused mass continually stirred until it reaches the ordinary temperature.

50 grams of this sample are saponified with 40 c.c. of caustic potash solution (D 1·4) and 40 c.c. of 96% alcohol. The soap is dissolved in a litre of water and boiled in a dish to expel the alcohol, the fatty acids being then separated by means of a slight excess of dilute sulphuric acid and the boiling continued until these acids form a perfectly limpid layer free from suspended clots. The aqueous liquid is siphoned off and the acids washed with hot water until they no longer give an acid reaction with methyl orange and then solidified by cooling. The disc of solid acids is melted on the water-bath, filtered through a dry filter in a boiling water-oven and the filtrate left overnight in a desiccator.

The setting point of the fatty acids thus obtained is ascertained as follows: A test-tube *b* (*see* Fig. 58) about 15 cm. long and 2 cm. internal diameter is filled to about two-thirds with the acids (about 30 grams) and heated in a water-bath until most of the substance is melted; the tube is then removed from the bath and the mass stirred with a glass rod until completely liquid (heating, if necessary, for a few moments). The tube is *then* fitted through the hole of the stopper *d* of a fairly wide glass cylinder

*a*, a thermometer *c*, reading to 0·2°, being arranged with its bulb exactly in the centre of the liquid mass. The whole is then left at rest.

The temperature is noted when the first crystals appear at the bottom of the tube, crystallisation then occurring at the surface of the liquid acids, on the walls of the tube and in the mass of the liquid. When numerous crystals appear throughout the liquid, the mass is stirred gently with the thermometer until it becomes pasty and opalescent and prevents the bulb of the thermometer from being seen (stirring for 12-15 seconds usually suffices); it is then left at rest.

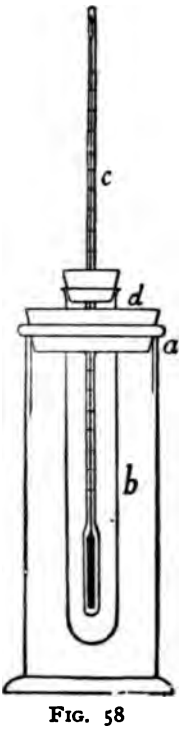

FIG. 58

Before and during the stirring the column of the thermometer is carefully observed. It falls at first slowly and regularly, but at a certain point the fall slackens, then stops, and towards the end of the agitation gives way to a rise to a maximum, the latter persisting for about two minutes. This stationary temperature represents the solidifying point (titer) of the fatty acids examined.[1]

The result is controlled by re melting—after some time (preferably 12 hours)—the fatty acids at a temperature not more than 5° above the solidifying point found and allowing the molten mass to solidify in the same conditions as before.

When the titer of a tallow is known, its yields of liquid acids (oleic) and solid acids (stearic and palmitic) may be deduced from *Dalican's Table* (XLVI), which has been compiled empirically by mixing a typical commercial stearine with solidifying point 54·4° with oleic acid freed from solid acids by prolonged standing and filtration. It indicates the percentages of stearic and oleic acids in a tallow, a deduction of 4% having been made for the glycerine and 1% for moisture and impurities.

The percentage of stearic or oleic acid in a mixture of fatty acids is given by the formula

$$\frac{a \times 100}{95},$$

where *a* is the percentage of stearic or oleic acid given in Dalican's table.

**2. Detection of Adulterations.**—(*a*) Bone and wool fats: by the odour. They lower the saponification number (especially wool fat) and if the unsaponifiable matter is extracted, this contains a considerable amount of cholesterol (*see* General Methods, 19).

(*b*) Palm oil and coco-nut oil; by the odour; they raise the saponification number, and the latter oil lowers the iodine number.

[1] In place of the arrangement indicated above, Shukoff uses a vacuum-jacketed vessel, into which 30-40 grams of the fused acid are poured. The vessel is then closed with a stopper carrying a thermometer, and when the first crystals appear the apparatus is shaken vigorously up and down until the contents become opaque. It is then left at rest and the maximum temperature reached by the thermometer noted.

### Dalican's Table

TABLE XLVI

| Solidification Point. | Stearic Acid % | Oleic Acid % | Solidification Point. | Stearic Acid % | Oleic Acid % |
|---|---|---|---|---|---|
| 35° | 25·20 | 69·80 | 44·5° | 49·40 | 45·60 |
| 35·5 | 26·40 | 68·60 | 45 | 51·30 | 43·70 |
| 36 | 27·30 | 67·70 | 45·5 | 52·25 | 42·75 |
| 36·5 | 28·75 | 66·25 | 46 | 53·20 | 41·80 |
| 37 | 29·80 | 65·20 | 46·5 | 55·10 | 39·90 |
| 37·5 | 30·60 | 64·40 | 47 | 57·95 | 37·05 |
| 38 | 31·25 | 63·75 | 47·5 | 58·90 | 36·10 |
| 38·5 | 32·15 | 62·85 | 48 | 61·75 | 33·25 |
| 39 | 33·45 | 61·55 | 48·5 | 66·50 | 28·50 |
| 39·5 | 34·20 | 60·80 | 49 | 71·25 | 23·75 |
| 40 | 35·15 | 59·85 | 49·5 | 72·20 | 22·80 |
| 40·5 | 36·10 | 58·90 | 50 | 75·05 | 19·95 |
| 41 | 38·00 | 57·00 | 50·5 | 77·10 | 17·90 |
| 41·5 | 38·95 | 56·05 | 51 | 79·50 | 15·50 |
| 42 | 39·90 | 55·10 | 51·5 | 81·90 | 13·10 |
| 42·5 | 42·75 | 52·25 | 52 | 84·00 | 11·00 |
| 43 | 43·70 | 51·30 | 52·5 | 88·30 | 6·70 |
| 43·5 | 44·65 | 50·35 | 53 | 92·10 | 2·90 |
| 44 | 47·50 | 47·50 | | | |

(*c*) Other vegetable oils: by the increase in the iodine number, by colour reactions, and by testing for phytosterol (*see* Hog's Fat).

(*d*) Cottonseed stearine: by Halphen's reagent (*see* Cottonseed Oil).

(*e*) Mineral substances (gypsum, talc and the like): detected in the portion insoluble in ether.

***

Pure tallows of good quality give about 95% of fatty acids setting at about 44°, the commercial valuation being made with 43·5° as basis; the saponification number is 195–200. They give a mean of about 9·5% of glycerine.

According to the Union of Italian Soap-makers, the titer of ox-tallow should not be below 43·5°, while that of mutton-tallow may vary from 41° to 49·8°. In different varieties the acidity allowed varies from 3% to 20%. Moisture and impurities allowed up to 1%.

## OLEOMARGARINE

This is the semi-fluid part expressed from tallow at about 25° or even a higher temperature. It is a soft yellowish fat, which readily decolorises in the light, has a faint odour of tallow and a slight agreeable taste.

It gives no appreciable colour reactions with the ordinary oil reagents, and its physical and chemical characters are as given below.

Oleomargarine serves as raw material for the preparation of artificial butter (*q.v.*, Vol. II, Chapter II).

The physical and chemical characters of oleomargarine are:

| | |
|---|---|
| Specific gravity at 15° | 0·924–0·930 |
| ,, ,, ,, 98–100° | 0·859–0·863 |
| Melting point | 32–35° (sometimes up to 40°) |
| ,, ,, of fatty acids | 40–43° |
| Solidifying point of fatty acids | 39–42° |
| Zeiss refractometric reading, at 35° | 50–52° |
| ,, ,, ,, ,, 40° | 47–49° |
| Acid number, if fresh and well stored | 0 |
| Saponification number | 192–200 (195–198) |
| Iodine number | 42–55 (43–48) |
| Fixed acid number | 95–96 |
| Volatile ,, ,, | 0·4–1·0 |

Under the polarising microscope it behaves like fused butter (*see* 3 in article on Butter, Vol. II, Chapter II).

## HOG'S FAT

Hog's fat is, strictly speaking, the fat of the inside of the animal, that adhering to the inside of the skin constituting *lard*.

American hog's fat is divided into various qualities according to the method of preparation.

In general the fat is white and pasty, with a peculiar odour and a sweetish taste; it becomes rancid easily, turning yellow. It is only slightly soluble in alcohol. With the ordinary reagents for oils it gives no colour reactions. Its characters are given in Table XLVII.

**Detection of Adulterations.**—Lard is adulterated with or even replaced by mixtures of tallow, pressed tallow (also hardened or hydrogenised oils), cottonseed stearine or other vegetable fats, or cottonseed, sesamé, arachis, maize, sunflower-seed, coco-nut or lard oil; also with pressed lard and vegetable oils. The artificial mixtures constituting *lard substitutes* often contain a small proportion of lard, recognisable mainly by its characteristic odour. Lards containing marked amounts of water, incorporated with the help of a little alkali, are also found.

The various adulterations are detected as follows:

1. WATER, ALKALI AND OTHER MINERAL SUBSTANCES. The water is determined by drying the fat at 100° to constant weight. Alkalis and other mineral matters may be found by incinerating the fat and examining the ash; the former may also be detected by treating with hot water and testing with litmus paper, or by passing a current of steam for half an hour into a mixture of 60 grams of the fat with 60 grams of water, then allowing the mass to cool and filtering: in presence of an alkali or an alkaline earth, a milky filtrate is obtained.

2. TALLOW, PRESSED TALLOW OR OTHER ANIMAL FAT OR HARDENED (HYDROGENISED) OIL. These substances are tested for by *Bömer's method*,[1]

[1] *Zeitschr. Unt. Nahr. Genussmittel*, 1913, XXVI, p. 559. *See also* papers on this method by Bömer, Alpers, Fischer and Werwerinke, and Sprinkmeyer and Diedrichs (*ibid.*, 1914, XXVII, pp. 142, 153, 361, 571).

based on the difference in the melting points of (1) the solid glycerides recrystallised from ether and (2) the fatty acids obtained from them.

(a) *Preparation of the glycerides.* In a beaker of about 150 c.c. capacity, 50 grams of the fused and filtered fat are dissolved in 50 c.c. of ether, the beaker being covered with a clock-glass, cooled to 15° and, with frequent shaking, allowed to crystallise. After an hour the mass is filtered through a funnel containing a perforated disc covered with a layer of filter-paper pulp, the liquid being pumped off and the crystalline mass left in the funnel then pressed with a watch-glass to free it from mother-liquor. The mass is then dissolved again in 50 c.c. of ether and after an hour filtered off as before.

The melting point of the glycerides thus obtained is usually 63–64° for pure lard, but lower if tallow is present. If the melting point is below 61°, the glycerides must be recrystallised from ether in the manner described until a portion melting at least as high as 61° is obtained. To judge with certainty, it is necessary that the glycerides melt between 61° and 65°.

To obtain a good crystallisation of the solid glycerides in the case of soft fats rich in liquid glycerides, the ethereal solution should be cooled to 5–10°, or use made either of a mixture of 3–4 parts of ether with 1 part of alcohol, or of anhydrous acetone.

(b) *Preparation of the fatty acids.* From 0·1 to 0·2 gram of the glycerides, m.p. 61–65°, is finely subdivided and placed in a beaker with 10 c.c. of about seminormal colourless alcoholic solution of potassium hydroxide. The liquid is boiled carefully for 5–10 minutes to bring about saponification, the soap being dissolved in 100 c.c. of water and the solution transferred to a separating funnel, decomposed with 2–3 c.c. of 25% hydrochloric acid and extracted with 25 c.c. of ether. The filtered ethereal solution is evaporated and the residue dried at about 100° for 30–60 minutes and, when cold, finely powdered.

(c) *Determination of the melting points.* The melting points of the glycerides and of the fatty acids prepared according to (*a*) and (*b*) are now determined under identical conditions. For this purpose, two very thin, perfectly similar U-tubes are used. With the help of a platinum wire, the finely powdered substance is introduced into one of the limbs of the U-tube so as to form a layer 2–3 mm. deep. The two tubes are then attached to a thermometer so that the branches containing the substances adhere to the bulb and the whole heated in a water-bath; when a temperature of 50° is reached, the heating is adjusted so that the rise in temperature is only 1·5–2° per minute. The temperature at which the layer becomes liquid, clear and transparent is taken as the melting point. The determination should be repeated with fresh substance and the mean of two concordant results taken.

With pure hog's fat the difference (*d*) between the melting points of the glycerides (M.G.) and of the fatty acids (M.A.), for values of M.G. lying between 61° and 65°, is never less than the values in the following table:

| M.G. | *d* | M.G. | *d* | M.G. | *d* |
|---|---|---|---|---|---|
| 61·0° | 5·00° | 62·5° | 4·25° | 64·0° | 3·50° |
| 61·5 | 4·75 | 63·0 | 4·00 | 64·5 | 3·25 |
| 62·0 | 4·50 | 63·5 | 3·75 | 65·0 | 3·00 |

For each 0·1° variation in M.G. the difference *d* changes by 0·05°, and the sum M.G. + 2*d* is never less than 71 with pure hog's fat. Hog's fat containing tallow of whatever origin or pressed tallow or hardened oil gives a lower value of *d* than is shown in the above table, while M.G. + 2*d* is less than 71.

EXAMPLES: A hog's fat gave: M.G. = 63·5° and M.A. = 58°, so that *d* = 5·5 and M.G. + 2*d* = 74·5°; the fat is thus pure.

Another fat gave: M.G. = 63° and M.A. = 60·5°, so that *d* = 2·5° and M.G. + 2*d* = 68. This fat contains tallow (pressed tallow, hardened oil).

3. VEGETABLE OILS AND FATS. COTTONSEED STEARINE. These adulterants are detected as follows:

(a) *Colour reactions.* Bellier's reaction (*see* General Methods, 23, 4) shows the presence of seed oils in general; Villavecchia and Fabris' reaction that of sesamé oil (*q.v.*); Halphen's reaction and the silver nitrate reaction according to Armani or Tortelli and Ruggeri, that of cottonseed stearine (*see* Cottonseed Oil).

Arachis oil is detected by the reaction for arachidic and lignoceric acids (*see* Arachis Oil).

(b) *Various characters.* Determinations are also made of the saponification, volatile acid and Polenske numbers (*see* General Methods, 8 and 10 of this chapter, and Butter, Vol. II), which detect the presence of coconut oil; of the ordinary and absolute iodine numbers (*see* General Methods, 12 and 13), which serve to confirm the presence of seed oils and to give an approximate indication of their quantity (when the nature of the vegetable oil has been ascertained); and of the rotatory power, for the detection of Hydnocarpus (Maratti) and Mowrah fats (*see* later, d).

As subsidiary determinations, measurements may also be made of the Zeiss refractometric reading at 40° (*see* Butter) and of the Maumené number (*see* General Methods, 21).

(c) *Detection of phytosterol.* This is of special importance in the analysis of lard, since only with its help can it be decided if vegetable oils have really been added.

Like all other animal fats and oils, hog's fat contains, as unsaponifiable substance, cholesterol (about 0·2% in the crude state), whereas the unsaponifiable substance of vegetable oils and fats consists of phytosterol. The crystalline form and the melting point of the unsaponifiable substances suitably purified (*see* General Methods, 19) and, better still, the melting point of their acetyl compounds serve to detect mixtures of cholesterol and phytosterol.

For the detection of phytosterol in lard (and, in general, in other animal

fats and oils), there are two suitable methods, the second being the more convenient.

(1) The *alcohol method*, according to Forster and Riechelmann[1]: 50 grams of the fat and 75 c.c. of 95% alcohol are boiled for 5–10 minutes in a flask fitted with a reflux condenser, the alcoholic liquid being separated while still hot and the boiling repeated with a further 75 c.c. of alcohol. The united alcoholic liquids, which contain the unsaponifiable substances, are boiled with 15 c.c. of 30% sodium hydroxide solution until saponification is complete, the liquid being evaporated almost to dryness and the residue extracted with ether. The ethereal solution is evaporated to dryness and the residue left taken up in a little ether, filtered and again evaporated. The final residue is dissolved in a little boiling 95% alcohol containing a few drops of dilute acetic acid and crystallised.

Repetition of the crystallisation from a little boiling absolute alcohol yields the *sterols* (cholesterol and phytosterol) ready for microscopic examination. With practice and by comparisons of mixtures of known composition, the crystalline form observed under the microscope indicates if the cholesterol is pure or mixed with phytosterol; the characteristic form of the latter is evident in mixtures containing only 5% of vegetable oil (*see* figures given under General Methods, 19).

The acetyl compound is then prepared as follows: All the crystals, together with the last mother-liquor, are freed from alcohol by heating in a glass dish on a water-bath, the residue being boiled for a moment with 3–5 c.c. of acetic anhydride, the dish being covered with a clock-glass meanwhile; the cover is then removed and the solution evaporated to dryness on a water-bath. The residue is dissolved in boiling absolute alcohol (about 20 c.c.) and the solution left to crystallise at the ordinary temperature. When about two-thirds of the alcohol have evaporated, the crystals are collected in a small filter and washed with 2–3 c.c. of 95% alcohol, the filter being then dried by pressing between filter-paper and the crystals redissolved in 5–10 c.c. of boiling absolute alcohol and left to crystallise. This operation is repeated three times. After the third crystallisation, the melting point of the crystals is determined, two further crystallisations followed by determinations of the melting point being carried out (*see* later).

(2) *Digitonin method*[2]: 50 grams of the fat are dissolved in about 120 c.c. of chloroform and the liquid heated on the water-bath at about 60° with 20 c.c. of a 1% solution of digitonin in 96% alcohol, with frequent shaking; it is then left at rest overnight. The cholesterol and phytosterol combine with the digitonin forming insoluble products (*digitonides*), which are deposited at the bottom of the chloroform solution of the fat. The liquid is filtered and the precipitate washed on the filter with chloroform and dried in the air.

[1] *Zeitschr. für öffentl. Chem.*, 1897, p. 10.

[2] This method may be applied under the conditions laid down by Marcusson and Schilling (*Chem. Zeit.*, 1913, p. 1001) or by Klostermann, Fritzsche, or Klostermann and Opitz (*Zeitschr. Unt. Nahr. Genussmittel*, 1913, XXVI, pp. 433, 614, and 1914, XXVII, p. 713). The method now described is deduced from these, with modifications found valuable as a result of tests made in the Italian Central Customs Laboratory by Dr. L. Settimj.

The digitonides thus obtained are boiled for 15–20 minutes, in a flask fitted with a reflux condenser, with about 20 c.c. of acetic anhydride, the liquid being then evaporated to dryness in a glass dish on the water-bath, the mass being stirred towards the end with a glass rod. The residue is recrystallised several times from 95–96% alcohol and the melting-point of the acetyl-compound thus obtained determined after the second, third or fourth crystallisation.

*Melting point of the acetyl-compound.* This is determined in a very thin glass U-tube, into one branch of which the powdered substance is introduced to form a layer 2–3 mm. deep. The observed melting point is then corrected by means of the formula,

$$x = \mathrm{T} + [n(\mathrm{T} - t) \times 0{\cdot}000154],$$

where $x$ = correct melting point,

T = observed melting point,

$n$ = length of mercury column of thermometer protruding from the bath, expressed in degrees,[1]

$t$ = mean temperature of the air about the protruding part of the thermometer, determined with another thermometer placed near the first and with its bulb at the middle of the protruding portion of the stem.[2]

The *corrected* melting point of cholesterol acetate is 114·3–114·8°, whilst that of phytosterol acetate is above 125°.

(d) *Rotatory power.* This is determined on the fat as such or on the unsaponifiable substances extracted from it. In the former case, which serves for the detection of Hydnocarpus oil, the rotatory power of the fat is determined in benzene solution at a temperature of about 20° with an ordinary shadow polarimeter. From the observed rotation the specific rotation $[\alpha]_D^{20}$ is calculated by means of the formula,

$$[\alpha]_D^{20} = \frac{100\alpha}{lc}$$

where $\alpha$ is the observed angle in circular degrees, $l$ the length in decimetres of the tube used, and $c$ the concentration, i.e., the number of grams of substance in 100 c.c. of the solution.

The determination of the rotatory power of the unsaponifiable substance is effected in the manner indicated by Berg and Angerhausen for the detection of Mowrah butter in lard.[3]

***

Genuine hog's fat should not contain appreciable quantities of water, alkaline substances or other mineral matters, and should be free from all extraneous fats and oils.

Its physical and chemical characters should lie within the limits given in Table XLVII. A saponification number above 200, volatile acid and Polenske numbers higher than 1, and an iodine number below 45 demonstrate the presence

[1] For instance, if the thermometer is immersed up to + 5° and the observed melting point is 115, $n = 115 - 5$.

[2] For melting points between 100° and 150°, $t$ = 50–56°.

[3] *Zeitschr. Unt. Nahr. Genussmittel*, 1914, XXVII, p. 723.

of coco-nut oil. Ordinary and absolute iodine numbers exceeding the limiting values yet observed show the presence of vegetable oils.

Its specific rotation should be very low and negative (about $-0{\cdot}06°$); if it is positive, the presence of Hydnocarpus oil (poisonous), which has the specific rotation about 55°, is assumed.

It should not contain arachidic and lignoceric acids.

It should not give any colour reaction for seed oils. It must, however, be borne in mind that a slight coloration may be given by lard from hogs fed with cottonseed, sesamé or other seed cake. In such cases, addition of seed oil to the lard is proved only when the presence of phytosterol is certain. This is the case when the acetyl-compound of the sterols obtained as described above has a corrected melting point higher than 115°.

Lard which gives the colour reactions but does not contain phytosterol cannot be regarded as containing vegetable oil.

The melting point difference, determined by Bömer's method, should be such that the value of M.G. + *2d* is 71 or more; if this value is less than 71, the lard is considered adulterated with tallow, pressed tallow or hardened oil.

In general, the following conclusions, based on the melting point difference and the phytosterol test, may be drawn [1]:

I. The melting point difference is normal: the lard is either pure or adulterated with vegetable oils. The phytosterol test (m.pt. of the acetyl-compound of the sterols) will demonstrate the presence or absence of vegetable oil.

II. The melting point difference is below the normal (M.G. + *2d* less than 71): the following cases present themselves:—

1. Phytosterol test negative: lard contains tallow, hardened animal oils or both.

2. Phytosterol test positive: there may be—

(*a*) Addition of vegetable oils or hardened oils;

(*b*) ,, of tallow (or pressed tallow) and vegetable oils or fats;

(*c*) ,, ,, ,, ,, ,, hardened vegetable oils.

## BONE FAT

This is obtained by de-fatting bones by means of water, steam or solvent (benzine, carbon disulphide). It varies in consistency but is usually soft and granular, and it has a yellowish or brown colour and a repulsive odour. It is somewhat soluble in alcohol, especially when it contains much free acid. The physical and chemical characters vary somewhat according as the fat is pure or has been extracted with solvents or steam; they are given in Table XLVII.

Bone fat contains cholesterol and, in accordance with the method of extraction, it may contain various impurities, such as water, lime soaps, gelatinous substances and hydrocarbons.

The analysis of bone fat for the purpose of determining its commercial value, includes the following:

**1. Determination of the Water.**—As indicated in the general methods, or more accurately by heating about 10 grams of the fat at 120° in a current of hydrogen to constant weight.

**2. Determination of Extraneous Impurities** (soaps, mucilaginous and gelatinous substances, etc.).—50 grams of the fat are well shaken with a quantity of ether sufficient to dissolve the fatty matter in the cold,

[1] Bömer: *Zeitschr. Nahr. Genussmittel*, 1914, XXVII, p. 158.

and left for some hours. The insoluble matter is collected on a weighed filter and washed with ether until the latter dissolves nothing further, the filter being then placed on a clock-glass, dried at 100° and weighed. The total impurity (gelatine, lime soaps, etc.) in the fat is thus determined.

If account is to be taken also of the fat combined as lime soap, treatment of the substance with ether is preceded by an hour's heating, with occasional shaking, on the water-bath with 3–5 drops of concentrated hydrochloric acid; the lime soaps having been decomposed in this way, the further procedure is as described above.

**3. Determination of the Ash.**—10 grams of the fat are carefully incinerated and the residue weighed. The ash of bone fat is composed of calcium oxide and a little carbonate, with small quantities of calcium phosphate, alumina and ferric oxide.

**4. Titer.**—As with tallow, the titer of bone fat is given by the solidifying point of the free fatty acids, this being determined as in the case of tallow (*q.v.*).

**5. Acid and Saponification Numbers.**—By the general methods, 7 and 8. The acidity is expressed as percentage of oleic acid.

**6. Hydroxy-acids.**—As in General Methods, 15.

**7. Unsaponifiable Substances.**—These may be estimated by saponifying the fat with alcoholic potash and extracting the aqueous solution of the soap with ether (*see* General Methods, 19).

**8. Recognition of Bone Fat which has been extracted with Benzine.**—According to Gianoli,[1] this may be effected as follows:

(*a*) The fat is subjected to prolonged distillation with concentrated calcium chloride solution; where the fat has been extracted with benzine, oily drops which are not soluble in soda float on the surface of the distillate.

(*b*) The fat is saponified with alcoholic sodium hydroxide, the alcohol expelled, the fatty acids liberated and washed with water, and this water treated in the hot with ammonia: turbidity indicates the use of benzine.

**9. Test for American Bone Fat.**[2]—To ascertain if a sample of bone fat of American origin may be used without inconvenience for soap-making, the following test is recommended:

100 grams of the fat and 30 c.c. of water are well shaken in a small steam-heated vessel with 20 grams of sulphuric acid (66° Baumé), the mass being afterwards heated and then left to stand: if the fat separates sharply and rapidly, it may be regarded as of good quality, but if an emulsion difficult to separate forms, the fat will give poor results and a bad yield of glycerine.

***

*Commercial bone fats* may have somewhat varying characters and composition: the water content usually ranges from 1 to 3%, but may reach even 20%; extraneous impurities vary from 0·5 to 3% and the ash also from 0·5 to 3%. The titer for good products is 36–44°, the acidity may exceed 50%, and the unsaponifiable matters usually lie between 0·5 and 2%.

The permissible limits for good bone fats for *soap-making* are: impurities, up to 3% (lime and magnesia soaps, iron, moisture, mucilaginous matter, higher

[1] *Ind. Sapon.*, 1909, p. 3. [2] *Ind. Sapon.*, 1914, p. 102.

alcohols, hydrocarbons, etc.); hydroxy-acids, up to 2%; acidity, not above 50%; saponification number, 185–195; titer, 36–42°.

## FOOT OIL

This is obtained more especially from the feet of the ox, but also from those of the sheep and horse. It is a pale yellow, almost odourless liquid, solidifying only below 0° (at about −5°). Its characters are indicated in Table XLVII.

**Detection of Adulterations.**—The oil may be adulterated with mineral, vegetable or marine animal oils, these additions being detectable by determining the various characters of the oil. Mineral oils lower the specific gravity and the saponification and iodine numbers and may be identified by investigation of the unsaponifiable substances (*see* General Methods, 19). Vegetable oils give Bellier's reaction and the other general reactions of seed oils (*see* General Methods, 23). By means of the special reactions and tests, colza, cottonseed and sesamé oils (*q.v.*) may be identified. Pure foot oil gives no colour reaction and does not contain arachidic and lignoceric acids or erucic acid. The presence of phytosterol would serve to confirm adulteration with vegetable seed oil (*see* Hog's Fat). Marine animal oils raise the specific gravity and the iodine number and may be identified by the special reactions indicated in the article on fish oils, etc.

***

For use as lubricants, foot oil should remain liquid and clear at 0° for a long time, should not contain more than 2% of free acids calculated as oleic acid, and should not contain extraneous oils. A drop lying in a thin film on a glass plate and kept at 50° for 24 hours should not resinify or dry up but should be easily removable from the glass.

# Fish and other Marine Animal Oils

These oils may be divided into three classes: (1) *Fish oils* proper, obtained from herrings, sardines, pilchards, sprats, tunny fish, shad, or from the residues obtained in the preparation of these fish; (2) *Blubber oils* (*train oils*), from the marine mammifers, the seal and whale; and (3) *Liver oils*, mainly from cod-liver but to a small extent from the liver of the ray, skate, etc.

Fish and blubber oils and cod-liver oil are treated separately in the two following articles; here, however, we shall give certain special reactions which are common to the three classes of oil and serve to distinguish all these oils from other fatty substances, either animal or vegetable.

**Characteristic Reactions.**—These reactions, which are now known to be trustworthy, are the following:

(*a*) Reaction of the Octabromo-compounds (given by Halphen, and modified by Lewkowitsch, Marcusson and Huber): From about 20 c.c. of the oil the fatty acids are extracted in the usual manner, 10 c.c. of the acids being then shaken vigorously, in a cylinder with a ground stopper,

## TABLE XLVII

## Characters of Terrestrial Animal Oils and Fats [1]

| Nature of the Fat. | Specific Gravity. t. | | Melting Point °C. | Solidifying Point °C. | Zeiss butyro-refractometer Reading. t°. | | Maumené Number (J = Jean, T = Tortelli apparatus). | Saponification Number. | Iodine Number. | Fixed Acid Number. | Volatile Acid Number. | Fatty Acids. Melting Point °C. | Fatty Acids. Solidifying Point °C. | Fatty Acids. Acetyl Number. | Fatty Acids. Iodine Number of the Liquid Acids. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bear's grease | 15 | 0·913 | — | 9 | — | — | — | 203–204 | 80–81 | — | — | — | — | — | — |
| Bone fat | 15 | 0·914–0·916 | 20–30 | 15–25 | — | — | — | 170–195 (185–190) | 44–75 (50 | 86–94 | — | 30–45 | 28–42 | 11–12 | — |
| Camel tallow | — | — | — | 34–35 | — | — | — | — | 36–39 | — | — | — | — | — | — |
| Duck (domestic) | — | — | 36–39 | 22–24 | — | — | — | — | 58–59 | — | — | — | — | — | — |
| Egg fat | 15 | 0·914–0·915 | 22 | 8–10 | 25 | 68–69 | 47–49 J | 184–192 | 64–82 | 95 | 0·4–0·7 | 34–39 | 30–35 | 12 | — |
| | 100 | 0·881 | | | | | | | | | | | | | |
| Fowl fat | 15 | 0·924 | 33–40 | 21–27 | — | — | — | 193–194 | 66–67 | — | 2 | 38–40 | 32–34 | 45 | — |
| Goose fat (domestic) | 15 | 0·922–0·930 | 25–34 | 18–22 | — | — | — | 191–198 | 58–71 | 92–96 | 1–2 | 37–41 | 31–38 | 27 | — |
| Hog's fat (*lard*) | 15 | 0·931–0·938 | 36–48 | 26–32 | — | — | 39–40 T | 195–200 (196) | 46–70 (60–66) | 95–96 | — | 35–47 | 34–40 | 2–6 | 92–105 |
| | 100 | 0·861–0·862 | | | | | | | | | | | | | |
| Horse fat | 15 | 0·918–0·933 | 25–39 | 20–30 | — | — | 53–54 T | 195–200 | 78–95 | 94–97 | 0·4–2 | 36–42 | 30–38 | 6–14 | — |
| | 100 | 0·861 | | | | | | | | | | | | | |
| Horse foot oil | 15 | 0·913–0·927 | — | below 0 | — | — | 58–59 T | 195–197 | 73–90 | — | — | 30–32 | 28–29 | 13 | — |
| Lard oil | 15 | 0·913–0·920 | — | —5 | 40 | 52 | 45–47 T | 191–196 | 69–83 (70–75) | 97–98 | — | 35 | 31 | — | — |
| | 100 | 0·826 | | | | | | | | | | | | | |
| Moose | 15 | 0·962 | 49–52 | 37–38 | — | — | — | 195 | 35 | — | 1–2 | 53–55 | 48–50 | 16–17 | — |
| Neat's foot oil (ox foot oil) | 15 | 0·914–0·919 | — | below 0 | 20 | 64 | 40–41 T | 189–200 | 64–78 | 95–96 | 1–2 | 28–35 | 26–27 | 22 | — |
| | 100 | 0·862 | | | | | | | | | | | | | |
| Ox marrow fat | 15 | 0·931–0·938 | 37–45 | 29–38 | — | — | — | 195–199 | 39–55 | — | 2 | 44–46 | 39–40 | 16 | — |
| Ox tallow | 15 | 0·943–0·953 | 40–49 | 27–37 | 40 | 44–49 | 31–42 T | 193–202 | 36–56 (40) | 95–96 | 0·5 | 43–48 | 38–47 (42–45) | 3–9 | 92–93 |
| | 100 | 0·860–0·863 | | | | | | | | | | | | | |
| Sheep's foot oil | 15 | 0·917–0·918 | — | below 0 | — | — | 41–52 T | 194–197 | 68–75 | 95 | 0·7 | 24–26 | 21–22 | — | — |
| Sheep's tallow | 15 | 0·937–0·961 | 44–52 | 32–41 | — | — | — | 192–197 | 32–46 | 95–96 | — | 45–55 | 40–48 | — | 92–93 |
| | 100 | 0·858–0·860 | | | | | | | | | | | | | |
| Silkworm chrysalis fat | 25 | 0·920–0·927 | — | 0–3 | 20 | 76 | — | 190–194 | 113–146 | — | 0·6 | 34–37 | 28–35 | — | — |
| | 40 | 0·910 | | | | | | | | | | | | | |
| Tallow oil | 15 | 0·916 | — | — | — | — | — | — | 55–57 | — | — | 34–39 | — | — | — |
| | 100 | 0·794 | | | | | | | | | | | | | |

[1] Numbers in brackets indicate the more common limits and mean values.

with 200 c.c. of Halphen's reagent (28 vols. of glacial acetic acid, 4 vols. of nitrobenzene and 1 vol. of bromine): a yellow precipitate of bromo-compounds is obtained. After an hour's rest, the liquid is filtered off by means of a pump and the precipitate washed with cold ether, powdered and boiled for half an hour in a reflux apparatus with benzene (50 c.c. of benzene per gram of precipitate): the octabromo-compounds of the fatty acids of marine animal oils remain undissolved by boiling benzene. The liquid is filtered through a steam-heated filter and the precipitate insoluble in benzene washed with boiling benzene, dried, and a determination made of its melting point, which should be above 190° (with incipient decomposition and blackening). If the melting point is below 190°, the precipitate is taken up several times with boiling benzene until a portion boiling above this temperature is obtained.

A reaction similar to the above is given also by the drying oils—linseed, walnut and hempseed oils (*see* Linseed Oil); the hexabromo-compounds furnished by these oils are, however, soluble in boiling benzene and melt at 175–180° without decomposing.

According to Marcusson, the octabromo-compound test—which is often made on the fatty acids and not on the oil as such—is able to detect 10% of marine animal oil mixed with linseed or other oil.

(*b*) TORTELLI AND JAFFE'S REACTION. In a graduated glass cylinder with a ground stopper, 1 c.c. of the oil, 6 c.c. of chloroform and 1 c.c. of glacial acetic acid are shaken together and 40 drops of a 10% solution of bromine in chloroform added; the cylinder is again shaken vigorously for a moment and then placed on a white paper and the colour of the liquid observed. Marine animal oils in general give a green coloration with a yellowish or blue reflexion, which increases during the space of half an hour and afterwards changes to brown. With vegetable or terrestrial animal oils and fats, pale yellow or yellowish colorations are obtained, these gradually darkening for an hour and then changing to brown.

For the reaction to succeed, the oil and the reagents must be perfectly dehydrated and the vessels very dry. If the oil is highly coloured, it may be decolorised with sulphuric acid [1] or soda.[2]

## FISH AND BLUBBER OILS

*Fish oils* proper are those obtained from the residues left during the preparation of various fish (sardines, herrings, shad, tunnyfish, etc.). From cetaceans are obtained mainly *Whale oil* and *Seal oil*, dolphin oil and porpoise oil being less common. In general these oils are liquid and often they are turbid and contain more or less abundant solid deposits; they

[1] 50 c.c. of the oil are treated for 5–6 hours, with occasional shaking, with 0·5 gram of conc. sulphuric acid and then filtered through a thin layer of fuller's earth: the filtrate is washed with boiling water to render it free from acid and filtered through paper in an oven at 100°.

[2] 100 c.c. of the oil and 5 c.c. of 30% caustic soda solution are heated on the water-bath for a quarter of an hour with frequent shaking, 50–60 c.c. of saturated sodium chloride solution being then added and the heating on the water-bath continued for three-quarters of an hour, with shaking. The oil is then decanted off, washed two or three times with hot water and filtered in an oven at 100°.

are coloured pale yellow to brownish red and have a more or less unpleasant odour. With alcoholic potash they mostly give brown soaps ; they contain small quantities of unsaponifiable substances (0·5–2%). When dissolved in carbon disulphide and treated with a little conc. sulphuric acid, they give a reddish-brown coloration with no trace of violet (*see* Cod-liver Oil). They give the general reactions for marine animal oils described above and their characters are given later in Table XLVIII.

Their analysis includes the following :

**1. Water, Impurities, Acidity.**—These are determined as in General Methods, 1 and 7.

**2. Distinction between Fish Oils and Blubber Oils.**—With pure oil of one kind or the other, the iodine and Maumené numbers are sufficient to determine if it is fish oil or whale (or seal) oil (*see* Table XLVIII). Mixtures of the two types of oil cannot be identified.

The reaction with carbon disulphide and sulphuric acid serves to distinguish fish and blubber oils from liver-oils (*see* following article).

**3. Detection of Impurities :**

(*a*) MINERAL AND RESIN OILS. These are detected by saponifying the oil (50–100 c.c.) and extracting and examining the unsaponifiable matter as indicated in General Methods, 19.

(*b*) VEGETABLE OILS. These are detected by the digitonin test for phytosterol (*see* Hog's Fat). Cottonseed and sesamé oil may also be identified by means of their special colour reactions, provided that the oil is not too much coloured.

## COD-LIVER OIL

This is obtained from the liver of *Gadus morrhua* and of other allied fish of the Northern Atlantic. According to its purity and colour it is divided into : *white* (medicinal, superior), which is clear, of pale or straw yellow colour, almost odourless and almost tasteless ; *pale*, which is clear, reddish-yellow, and with a marked fishy odour and taste ; *red* or *brown*, which is more or less turbid and brownish-red and with an unpleasant fishy odour and taste.

It dissolves slightly in alcohol, but easily in ether, benzene or other ordinary fat solvent. It contains small quantities of unsaponifiable substances (mainly cholesterol) : 0·3–2% in pale oils and up to about 8% in crude brown ones.

Further it contains traces of iodine in organic combination (0·0002–0·04%). This is not extractable by solvents or by mere saponification, but is detected only by saponifying the oil, adding a little nitre to the soap, evaporating to dryness, incinerating and carefully calcining and testing the ash for iodine in the usual way.

It gives the general reactions of marine animal oils described above, and its characters and those of the livers of other fish are given in Table XLVIII. The determinations to be made are :

**1. The Special Reaction** for this oil, but common to all others from fish-livers, is as follows : A drop of the oil is dissolved in 2 c.c. of carbon

## TABLE XLVIII
## Characters of Marine Animal Oils [1]

| | Specific Gravity. | Setting Point. | Zeiss Butyro-refracto-meter Reading. | Maumené Number (J = Jean, T = Tortelli apparatus). | Saponi-fication Number | Iodine Number. | Fixed Acid Number. | Volatile Acid Number. | Fatty Acids. Melting Point. | Fatty Acids. Setting Point. | Fatty Acids. Acetyl Number. | Fatty Acids. Iodine Number of the Liquid Acids. | Unsaponi-fiable Substance % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FISH OILS | | | | | | | | | | | | | |
| Menhaden (*Alosa menhaden Cuv.*) | 0·927–0·933 (15°) | – | 71–72 (40°) | 123–128 J | 188–193 | 160–179 | — | 2–3 | — | — | — | — | 0·6–2 |
| Herring (*Clupea Harengus*) . . | 0·920–0·939 (15°) | — | — | — | 170–194 | 103–142 | 95–96 | — | 30–32 | — | — | — | 1–2 |
| Japanese sardine (*Clupanodon melanostica* T. S.) | 0·928–0·935 (15°) | — | — | — | 189–196 | 160–190 | 95–97 | — | 35–36 | — | — | — | 0·5–2·6 |
| Indian sardine . . . . . | 0·875–0·878 (100°) | — | — | — | 193–200 | 154–159 | — | — | — | — | — | — | — |
| European sardine (*Clupea sardinus*) | 0·928–0·934 (15°) | 20–22° | — | 112–113 T | 189–196 | 160–193 | 94–96 | — | 30–31 | — | 21–22 | — | 0·5–0·9 |
| Sprat (*Clupea sprottus*) . . . | 0·927–0·928 (15°) | — | 76 (25°) | — | 194–195 | 122–142 | 95 | 1–2 | 28 | 25–26 | 8–9 | — | 1–2 |
| Tunny (*Thynnus vulgare, T. Schlegeli*) | 0·932–0·933 (15°) | — | 89 (20°) | — | 185–186 | 156–199 | 95–96 | — | 31 | — | 22–29 | — | 1–2 |
| LIVER-OIL OF | | | | | | | | | | | | | |
| Cod (*Gadus morrhua*) . . . . | 0·920–0·938 (15°) | below 0° | 75–85 (25°) | 102 T | 171–193 (185–190) | 135–182 (150–170) | 95–97 | 0·2 | 21–25 | 13–24 | 19–51 | — | 0·3–8 |
| Dog-fish (*Squalus spec.*) . . . | 0·910–0·929 (0·915–0·917) (15°) | — | — | 90 J | 146–183 (160) | 90–138 | 97–98 | 1–2 | — | — | 66 | — | 10–21 |
| Ray (*Raya batis, R. Clavata*). . | 0·931 (15°) | — | — | — | 185–186 | 157 | 94–95 | 1 | — | — | 10–11 | — | 1 |
| BLUBBER OILS | | | | | | | | | | | | | |
| Whale (*Balæna mysticetus, B. Australis*) | 0·916–0·930 (15°) 0·872 (100°) | — | 65 (25°) | 75–76 T | 160–202 (180–190) | 90–146 | 93–95 | 1–4 | 14–27 | 10–24 | 11–23 | 148 | 1–4 |
| Dolphin, from the body (*Delphinus globiceps*) | 0·918–0·930 (15°) | — | 65–69 (20°) | — | 197–231 | 99–127 | 93 | 11–44 | — | — | — | — | 2 |
| Do., from head and jaw . . . | 0·924–0·926 (15°) | — | 39–40 (20°) | — | 277–290 | 24–33 | 66 | 112–132 | — | — | — | — | — |
| Seal (*Phoca spec.*) . . . . . | 0·924–0·930 (15°) 0·873 (100°) | below 0° | 72–73 (25°) | 72 T | 178–196 | 118–160 | 94–96 | 0·1–0·4 | 14–31 | 13–26 | 25–34 | — | 0·3–1 |
| Shark (*Orca gladiator*). . . . | — | — | — | — | 208–258 | 63–92 | — | 24–88 | — | — | — | — | — |
| Otaria (*Otaria Stelleri*) . . . | 0·928 (15°) | — | 80 (20°) | — | 189–190 | 156–157 | — | — | 29 30 | — | — | — | — |
| Porpoise, from the body (*Delphinus phocaena*) | 0·926 (15°) 0·871 (100°) | — | — | — | 195–219 | 119–120 | — | 22–24 | — | — | — | — | — |
| Do., from head and jaw . . . | 0·926 (15°) | - - | — | — | 253–272 | 21–50 | 68–72 | 94–132 | — | — | — | — | 16–7 |

[1] The numbers in brackets indicate the more common limits and mean values.

disulphide and the solution gently shaken with a small drop of conc. sulphuric acid : a fine purple-violet coloration, rapidly changing to brownish-red, is obtained.

Other marine animal oils, treated similarly, give no violet coloration (*see* preceding article).

**2. Acid Number.**—As in General Methods, 7.

**3. Test for Added Iodine (Inorganic).**—About 10 c.c. of oil are shaken with as much water, the latter being then separated and treated with starch paste and either conc. nitric acid or chlorine water : appearance of a blue coloration indicates inorganic iodine.

**4. Freezing Point.**—The oil is maintained at 0° for some time to ascertain if it remains liquid.

**5. Detection of Adulterations.**—The oil may contain the following admixtures :

(*a*) OTHER FISH-LIVER OILS. No certain methods are known of distinguishing different fish-liver oils or their mixtures.

(*b*) FISH AND BLUBBER OILS. No certain method exists of detecting fish-oil in cod-liver oil. Addition of blubber oil (whale, seal) may be suspected as a result of determinations of the iodine number, the Maumené number and the refractometer reading (Zeiss), which are lowered by whale or seal oil (*see* Table XLVIII).

(*c*) VEGETABLE AND MINERAL OILS. These are recognised by the methods given in the preceding article (Fish and Blubber Oils).

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According to the Official Italian Pharmacopœia, *medicinal* cod-liver oil is amber or straw-yellow, D at 15° = 0·922–0·930, iodine number = 150–170. When cooled to 0° it does not congeal, but deposits flocks of white solid matter. It should give the reaction for fish-liver oils and should contain no inorganic iodine (test 3).

The acidity is low in white oils, especially in so-called steam liver oil (0·3–2% as oleic acid), but is higher (up to 8%) in the more highly coloured yellow or pale oil and may reach about 30% in brown oils.

## Waxes

Waxes are composed essentially of compounds of certain fatty acids (palmitic, stearic, cerotic) with higher alcohols (cetyl, myricyl alcohols) ; some contain also a certain amount of free acids (beeswax, carnauba wax) and solid hydrocarbons (beeswax). Waxes are of animal origin, such as beeswax, Chinese insect wax, wool fat and spermaceti, and of vegetable origin, such as carnauba wax, fig wax, ocuba wax, etc. The latter should not be confused with other vegetable products known as waxes, these being really fats, such as Japan wax and myrtle wax (*see* Vegetable Fats).

The waxes of greatest importance are : beeswax, wool fat, spermaceti and the corresponding oil, which are dealt with in detail. Of the other waxes the characters are given in Table XLIX.

## BEESWAX

*Crude* (*virgin*) wax in pale yellow or brown. European qualities are yellow or pale yellow, the African and American reddish-yellow to brown, and the Indian greyish-brown. It is fatty to the touch and soft and plastic to the heat of the hand, and presents a granular fracture. It has a special odour, recalling that of honey, and a faintly balsamic taste.

*White or bleached* wax (decolorised by air and light or by chemical means) is white, brittle, and only slightly fatty and odoriferous.

In general the wax is almost insoluble in cold alcohol but partly soluble in boiling absolute alcohol, from which it separates on cooling. It is slightly soluble in cold ether, more so in boiling ether, chloroform or benzene.

It consists principally of cerotic acid and myricyl palmitate (myricin), but contains also free melissic acid and ceryl alcohol and hydrocarbons (3–12%, according to the origin).

The physical and chemical characters of different types of beeswax are given in Table XLIX.

The wax may be adulterated with stearine, colophony, paraffin wax or ceresine, Chinese (insect) wax, carnauba wax, Japan wax (so-called), tallow, wool fat, flour or starch, and mineral substances; water may also be present. The colour may be enhanced by turmeric or coal-tar colours.

Imitations of the wax are made with paraffin wax, ceresine and colophony, or with various mixtures of paraffin wax, carnauba wax, Japan wax, stearine, etc., often coloured with coal-tar colours.

To detect the different adulterations and imitations here indicated, it is necessary to determine the various characters (*see* 1–5) and further to apply certain special tests (*see* 6–13), since it is possible to prepare mixtures with the characters of the pure wax. If, on the other hand, the detection of beeswax in mixtures with other substances is required, test 14 is employed.

In the case of the crude (virgin) wax, before proceeding to the analysis (with the exception of the determinations 12), it is well to boil the sample with water to remove the whole of the honey and then to filter the fused mass in the hot.

**1. Specific Gravity.**—This may be determined most exactly by means of the specific gravity bottle, but Hager's method may also be used. The wax is melted at a gentle heat and poured in drops into cold 70% alcohol, the beads of wax thus obtained being dried in absorbent paper, left overnight to solidify and then immersed in alcohol of known specific gravity, e.g., 0·965, at 15°. If the beads remain suspended at any point of the liquid, the specific gravity of the wax is that of the liquid, i.e., 0·965; if, on the other hand, they sink or float, tests are made with more dilute or more concentrated alcohols until the correct specific gravity is obtained. It is usually sufficient to prepare eight or ten alcohol solutions with specific gravities from 0·960 upwards.

It is also desirable to determine the specific gravity of the wax at 98–100° (*see* General Methods, 3).

**2. Melting Point.**—As in General Methods, 4.

**3. Acid and Saponification Numbers.**—These may be determined

as in General Methods (7 and 8), the titration of the free acids being made on the hot (almost boiling) alcoholic solution of the substance with a standard *alcoholic* potassium hydroxide solution (about seminormal), while for the determination of the saponification number the substance is boiled with the alcoholic solution for at least two hours on an asbestos card over the naked flame, the wax being difficultly saponifiable.

More exact determinations may be made by Berg's method, modified by Bohrisch and Kurschner : about 4 grams of the wax, 20 c.c. of xylene (recently distilled) and 20 c.c. of absolute alcohol (neutralised) are boiled in a reflux apparatus for 5–10 minutes ; titration of the liquid with seminormal alcoholic potash (with phenolphthalein) gives the acid number. A further quantity of 30 c.c. of the same potash solution is then added, the liquid boiled for an hour, treated with 50–75 c.c. of 96% alcohol (neutralised), heated for 5 minutes longer, and the excess of potash titrated with seminormal hydrochloric acid (indicator as above) ; the ester number is thus obtained.

In judging a wax (*see* later) it is important to know the acid, saponification and *ester numbers*, the last being the difference between the first two.

The ratio of ester number to acid number, the so-called *ratio value*, is also of importance.

**4. Iodine Number.**—As in General Methods, 12.

**5. Refractometric Reading.**—This is determined with the Zeiss butyro-refractometer (*see* Butter, Vol. II, Chapter II) at a temperature of 64°. To reduce the reading to the normal temperature of 40°, the difference between 64 and 40, i.e., 24, is multiplied by 0·53 and the product added to the reading at 64°.

**6. Test for Stearine.**—About 3 grams of the wax and 10 c.c. of 85% alcohol are heated and shaken in a flask until the wax is thoroughly fused and then left to cool for some hours with frequent shaking ; only the stearine (and also any resin, *see* later, 7) remains in solution. The solution is then filtered and the filtrate diluted with a large amount of water. With the pure wax the liquid remains clear, whereas the presence of stearine (about 1% or more) produces a marked turbidity or a white precipitate, which may be collected and identified by means of its melting point (53-55°) and saponification number (about 195), provided of course that Morawski's reaction indicates that resin is absent.

When resin and other extraneous acid substances soluble in alcohol are absent, the stearine (S) added to a wax may be calculated from the acid number found ($a$) by means of the formula :

$$S = \frac{100(a - 20)}{175}.$$

When a wax or a mixture resembling wax contains stearic acid and resin, it is well to eliminate these substances immediately by means of 85% alcohol and to make the other tests and determinations on the insoluble residue.

**7. Resin (Colophony).**—From 3 to 4 grams of the wax are heated with dilute alcohol (about 80%), the mass being allowed to cool and filtered,

the filtrate evaporated and the residue employed for the detection of resin by means of acetic anhydride and sulphuric acid (*see* General Methods, 20).

The quantitative determination may be effected by Twitchell's method (*see* General Methods, 20).

**8. Paraffin Wax and Ceresine.**—As a preliminary test, 5 grams of the wax, about 25 c.c. of seminormal alcoholic potassium hydroxide and 20 c.c. of 95% alcohol are boiled for an hour in a reflux apparatus over a naked flame : with pure wax the solution is clear, or almost clear, and remains so when diluted with hot water, but with wax mixed with paraffin wax or ceresine, the liquid remains turbid, and becomes still more so when diluted with water.[1]

A more certain and even *quantitative* test may be made by Leys' method[2] : 10 grams of the wax, 25 c.c. of alcoholic potash (45 grams KOH per litre of absolute alcohol) and 50 c.c. of pure benzene are boiled for 20 minutes in a reflux apparatus on an asbestos card over a naked flame, 50 c.c. of water being then added and the boiling continued for 10 minutes. After a short rest, the liquid separates into two layers : an upper, clear, yellowish one (benzene solution of higher alcohols and hydrocarbons) and a lower, somewhat opalescent one (aqueous-alcoholic soap solution). As soon as the separation is sharp, the lower hot liquid is drawn off and replaced by 50 c.c. of hot water, and the liquid boiled for 10 minutes with a reflux apparatus. The aqueous solution is then immediately withdrawn and the benzenic liquid transferred to a tared capsule, the various vessels in which the operations have been conducted being washed out with hot benzene[3] ; the solvent is then evaporated on the water-bath and the residue dried at 100° and weighed. This gives the total weight of higher alcohols and hydrocarbons contained in the wax and from this the content of extraneous hydrocarbons may be deduced, knowing that in pure wax the sum of alcohols and hydrocarbons never exceeds 55% (usually oscillating about 50%).

If desired, the hydrocarbons may, according to Leys, be separated quantitatively from the higher alcohols by means of a mixture of amyl alcohol and conc. hydrochloric acid, in which the latter dissolve (*see* original paper) ; or, as Buchner recommends,[4] the acetyl number (*see* General Methods, 11) of the mixed higher alcohols and hydrocarbons may be determined and the quantity of the former deduced by taking 122 as the mean acetyl number of the higher alcohols of the pure wax.

**9. Test for Carnauba Wax and Insect or Chinese Wax.**—No special reactions exist for identifying these waxes in beeswax ; when, however, the presence of other extraneous substances has been excluded and any stearic acid and resin eliminated as indicated above (6), their presence may be presumed from increase of the specific gravity, melting point,

[1] Werder : *Monit. scient.*, 1901, p. 127.

[2] *Journ. de Pharm. et Chim.*, 1912, V, p. 577.

[3] Very suitable for this purpose is a special vessel (*Boule à decantation chaude*) devised by Leys and consisting of a tapped funnel flattened on one side so that it may be heated like an ordinary flask.

[4] *Zeitschr. f. öffentl. Chem.*, 1913, p. 447.

refractivity and ratio value (*see* above) and from diminution in the acid number (*see* later).

**10. Test for Japan Wax** (from various species of *Rhus*), **Tallow and other Fats in general.**—A scrap of fused potassium bisulphate is added to about 1 gram of the molten wax in a test-tube and the mixture strongly heated over a direct flame : the pure wax gives pungent sulphurous fumes, whereas in presence of fats (glycerides) the characteristic irritating odour of acrolein (due to decomposition of the glycerine) is observed and a strip of filter-paper, soaked in a solution of sodium nitroprusside and a little piperidine and placed at the mouth of the tube, turns violet-blue.

If this test shows the presence of glycerides, the glycerine is determined as in General Methods, 17 ; the amount of glycerine, multiplied by 10, gives approximately the quantity of fatty substance in the wax, since fats contain on the average about 10% of glycerine.

It should also be borne in mind that Japan wax, tallow and other fats lower the melting point and raise the saponification number (tallow raises also the iodine number) of the wax (*see* later).

**11. Detection of Wool-Fat and its Products (Wool-Fat Stearine or Wax).**—The higher alcohols and hydrocarbons are extracted from the wax by Leys' method (8), the mixture thus extracted being tested for cholesterol by means of chloroform and sulphuric acid (*see* General Methods, 19, Higher Alcohols).

**12. Determination of the Water and Various Extraneous Impurities.**—About 5 grams of the wax as it stands are heated at 100–105° to constant weight, the loss representing the water. The residue is dissolved in hot benzene and the solution filtered from any appreciable undissolved portion through a tared filter, the insoluble matter being washed well with hot benzene, dried at 100° and weighed.

The residue insoluble in benzene is then tested for starchy or mineral matters by the usual methods.

**13. Extraneous Colouring Matters.**—About a gram of the rasped wax is shaken with ammonia : in presence of *turmeric*, a reddish-brown coloration is obtained.

To detect *coal-tar dyes*, the wax is extracted with 90–95% alcohol in the hot. The liquid is then cooled well at 15° for some hours and filtered, the filtrate being evaporated and tested for artificial colouring matters (*see* Coal-tar Dyes in Vol. II). As a rule imitation wax and wax substitutes are coloured with the so-called Soudan dyes, which are turned pink with conc. hydrochloric acid.

**14. Detection of Beeswax in Mixtures with other Substances.**—To ascertain if wax is contained in wares of different kinds, such as paraffin wax, fats, candles, artificial fruit and flowers, lithographic stones, mastics, encaustics, ointments, plasters, waxed paper and cloth, myricyl alcohol is tested for. This may be done indirectly by means of the acetyl number, or by transforming the alcohol into melissic acid. The test is, however, practicable only when other substances containing higher alcohols, such as wool-fat and its products, are excluded. Carnauba wax, which also con-

tains myricyl alcohol, behaves like beeswax, and the same holds with Chinese insect wax, which contains ceryl alcohol.

(*a*) By means of the Acetyl Number. The substance [1] is saponified and the unsaponifiable part extracted by the usual methods or preferably by Leys' method (*see* 8) and its acetyl number determined (*see* General Methods, 11). If this number is found to be zero, the presence of the wax may be excluded; if, however, there is an acetyl number, the presence of the wax may be assumed and the amount may be calculated approximately from the fact that the mean acetyl number of the higher alcohols of the wax is 122 and that the wax contains, on the average, about 40% of higher alcohols.

(*b*) By transformation of the Myricyl Alcohol into Melissic Acid. 5 grams of unsaponifiable substance, extracted as for the preceding test, are intimately mixed with about 10 grams of powdered soda lime and a little caustic soda, the mixture being placed in a large test-tube and this plunged into a sand-bath and heated to 200–220° for 2 hours; the temperature is measured with a thermometer immersed in the substance and used at intervals as a stirrer. When cold, the substance is extracted with petroleum ether, the solvent evaporated and the residue weighed. If the weight is equal or nearly equal to that of the substance used, the presence of wax is excluded, but if the petroleum ether extract is appreciably less in weight than the substance taken, wax may be present. In the latter case the difference between 5 grams (weight of substance used) and the weight of the residue represents the myricyl alcohol contained in the 5 grams of unsaponifiable matters. If, then, the percentage of unsaponifiable matter in the substance is known, the myricyl alcohol contained in 100 parts of the substance itself and hence approximately the percentage of the wax present may be calculated, since 38 parts of myricyl alcohol correspond on the average with 100 parts of beeswax.

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The purity of a wax is judged first of all from the results of the determinations of the various characters, account being naturally taken of the origin and nature of the wax: if all or some of these characters lie outside the limits indicated in Table XLIX, the wax is not genuine.

A low specific gravity indicates the presence of solid paraffin or ceresine, stearic acid or tallow, and a high one that of carnauba wax, Japan wax or colophony.

The acid, saponification, ester, ratio, iodine and refractometric numbers are also influenced more or less by the presence of various foreign substances, as is shown in the following table (page 439), where the mean characters of ordinary virgin wax are compared with those of the substances most usually employed to adulterate it.

It should, however, be noted that mixtures may be prepared, with or without beeswax, so as to have the characters given above for the pure wax. Consequently, if it is certain that a wax is adulterated if its characters are abnormal, normal characters do not necessarily correspond with a pure wax; in the latter case, tests 6–11 must be carried out.

[1] In the case of plasters or waxed paper or cloth, the sample is extracted with boiling benzene, the liquid filtered and evaporated and the residue examined.

| | Specific Gravity at 15° C. *a* | Melting Point *b* | Acid Number *c* | Saponification Number *d* | Ester Number *e* | Ratio Value *f* | Iodine Number *g* | Refractometric Degree at 40° C. *h* |
|---|---|---|---|---|---|---|---|---|
| Beeswax . . | 0·964 | 63° | 20 | 95 | 75 | 3·70 | 10 | 44 |
| Insect wax . . | 0·970 | 82° | 0 | 63 | 63 | 63 | — | 46 |
| Carnauba wax . | 0·995 | 85° | 4 | 79 | 75 | 18·75 | 10 | 66 |
| Japan wax . . | 0·990 | 53° | 20 | 220 | 200 | 10 | 9 | 47 |
| Stearine. . . | — | below 55° | 195 | 195 | 0 | 0 | — | — |
| Tallow . . . | 0·948 | 42° | 4 | 195 | 191 | 48 | 40 | 47 |
| Resin (colophony) | 1·100 | above 70° | 180 | 190 | 10 | 0·06 | 115 | — |
| Solid paraffin . | 0·870 | below 65° | 0 | 0 | 0 | 0 | 0 | 22 |
| Ceresine. . . | 0·920 | above 60° | 0 | 0 | 0 | 0 | 0 | 40 |

## WOOL FAT

This is obtained from wool by washing with soap or alkali carbonate solution or by extracting with a solvent (carbon disulphide or benzine).

The crude fat is utilised especially for the preparation of lanoline and distilled wool fat, from which wool fat oleine and stearine are prepared. The latter products are dealt with in the next chapter (Industrial Products from the Treatment of Fatty Matters); here we shall deal only with crude and purified wool fat and lanoline.

### *A.* Crude Wool Fat

This has a tallowy consistency, a yellow or brown colour, and a peculiar, disgusting odour. It is slightly soluble in alcohol, and more so in ether, chloroform, benzene, etc.; it saponifies with difficulty. Its physical and chemical characters are given later in Table XLIX, dealing with animal waxes. It is dextro-rotatory ($[\alpha]_D^{35°}$ = about 6-9° in chloroform solution), and its acid number may vary from about 10 to 50 (5-25% of free acids calculated as oleic acid) according to the method used in its extraction. On calcination it leaves little ash (1-5%).

It contains marked quantities of unsaponifiable substances (40–50%), consisting mainly of cholesterol and isocholesterol, and consequently gives the reaction of these higher alcohols with chloroform and sulphuric acid (*see* General Methods, 19, 1, Higher Alcohols). It may also contain water and various foreign impurities in varying quantities.

Crude wool fat is readily identified by its external characters and by the cholesterol reaction. In analysing it, it is usually sufficient to determine the content of water, extraneous impurities, and ash, with possibly the acid number and the unsaponifiable matter, by the usual methods (*see* General Methods).

### *B.* Purified Wool Fat (Lanoline)

*Purified wool fat* is pale yellow and sticky, has a faint, peculiar smell and the consistency of an ointment and undergoes little change in the air.

It gives stable mixtures or emulsions with large quantities of water (up to more than 100%), and the fat mixed with 20–30% of water is given the name *Lanoline.*

It dissolves little in cold alcohol and somewhat more in boiling absolute alcohol; it is soluble in ether or chloroform, giving, however, turbid liquids when it contains water. Its characters are indicated in Table XLIX.

When a solution of 0·1 gram of dehydrated lanoline in 5 c.c. of chloroform is carefully poured on to 5 c.c. of conc. sulphuric acid, at the zone of contact of the two liquids there is produced a bright brownish-red coloration, which reaches its maximal intensity after 24 hours.

The most important tests to be made on *lanoline,* especially that for pharmaceutical purposes, are:

**1. Water and Ash.**—10 grams are heated at 100–110° to constant weight, the residue being carefully incinerated and the ash weighed.

**2. Acidity.**—As in General Methods, 7.

According to the Official Italian Pharmacopœia, the test for acidity is made by dissolving 2 grams of the lanoline in 20 c.c. of petroleum ether, adding 2 drops of phenolphthalein solution and then 0·5 c.c. of decinormal sodium hydroxide solution: the liquid should be coloured a persistent red.

**3. Other Tests.**—The lanoline is heated with aqueous caustic soda solution to ascertain if ammonia is evolved. 10 grams of lanoline are heated on the water-bath with 50 grams of water: a clear and slightly coloured layer of fused fat should form at the surface of the water; with impure lanoline a brown, turbid and frothy mass is obtained.

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Pure anhydrous lanoline should contain only traces of moisture, and that emulsified with water should contain not more than 30% of the latter. Further, it should have little ash (at most 0·05%), give no acid reaction with litmus paper, correspond with the Official Italian Pharmacopœia test (2), and give no ammonia when heated with soda solution.

## Spermaceti.

This is the solid portion obtained by cooling and pressure from the oil contained in the cephalic cavity of the sperm whale or cachalot (*Catodon macrocephalus*) and allied species.

Refined or pure spermaceti of commerce is in white, hard, crystalline masses (thin sheets), slightly fatty to the touch and almost odourless; in the air it becomes yellowish and rancid.

It dissolves in boiling alcohol, from which it crystallises on cooling, and it is soluble also in ether, chloroform, benzene and carbon disulphide; it dissolves very slightly in cold 98% alcohol and is insoluble in 90% alcohol or in water. Its physical and chemical characters are given in Table XLIX.

Spermaceti consists mostly of *cetin* (the cetyl ester of palmitic acid), m.pt. 53·5°, and contains 50–52% of unsaponifiable substances.

**Detection of Adulterants.**—Additions of ceresine or solid paraffin, stearic acid (stearine), tallow and beeswax are made, but only rarely, since extraneous substances easily destroy the characteristic crystalline structure.

## TABLE XLIX
## Characters of Waxes [1]

| Nature of Wax. | Specific Gravity. t° | | Melting Point °C. | Solidifying Point, °C. | Zeiss Butyro-refractometer Reading. t° | | Acid Number A | Saponification Number. | Ester Number E | Ratio Value E/A | Iodine Number. | Unsaponifiable Substances % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **ANIMAL WAXES** | | | | | | | | | | | | |
| Crude ordinary beeswax (*Apis mellifera*) | 15 | 0·941–0·976 (0·964) | 60·5–66·5 (63) | 60–61 | 40 | 43·2–45·7 (44) | 16·7–23·6 (20) | 88–106 (95) | 65·9–85·0 (75) | 2·8–4·5 (3·7) | 5·7–17·1 (10) | 48–53 |
| Do., bleached in the sun | 15 | 0·964–0·973 (0·966) | 63–64 | 61–62 | 40 | 44 | 19–23 (20) | 90–98 (95) | 71–76 (75) | 3·7 | — | — |
| | 100 | 0·818–0·827 | | | | | | | | | | |
| Do., bleached chemically | — | — | 63–64 | 61–62 | — | — | 16·8–24 | 93–108 | 71–84 | 3–4 | 1–11 | — |
| Do., pressed | — | — | — | — | — | — | 21–22 | 81 | 59–60 | 3 | — | — |
| Do., extracted (with solvents) | 15 | 0·949–0·984 | 59–72 | — | — | — | 15–28 | 64–102 | 49–78 | 2·4–3·4 | — | — |
| Indian beeswax (Ghedda wax), crude (*Apis dorsata, A. florea, A. indica*) | 15 | 0·966 | 60–69 (63–64) | — | 40 | 44–46 | 5–13 (7–8) | 75–145 (100) | 70–124 (93) | 7–18 (13) | 3–12 (8–9) | — |
| Insect wax (Chinese wax) (*Coccus ceriferus*, Fabr.) | 15 | 0·926–0·970 (0·970) | 81–83 | 80–81 | 40 | 46 | 0 | 63–93 (63) | 63–93 (63) | 63 | 1–2 | 49–50 |
| | 100 | 0·810 | | | | | | | | | | |
| Wool fat, crude | 15 | 0·973 | 39–42 | — | — | — | 10–50 | 77–146 | — | — | 20–35 | 40–50 |
| Do., purified (Anhydrous lanoline) | 15 | 0·978 | 36–42 | 38–40 | — | — | 0–1 | 98–127 (100) | — | — | 10–29 | — |
| | 100 | 0·901–0·902 | | | | | | | | | | |
| Spermaceti | 15 | 0·940–0·960 | 44–55 | 43–48 | — | — | 0–5 | 108–135 | — | — | 5–9 | 50–54 |
| | 100 | 0·808–0·842 | | | | | | | | | | |
| Spermaceti oil | 15 | 0·875–0·890 | — | — | 25 | 54 | — | 117–150 (132) | — | — | 62–90 (80–82) | 37–42 |
| | 100 | 0·833 | | | | | | | | | | |
| Bottlenose oil (Arctic sperm oil) (*Hyperoodon rostratus*) | 15 | 0·876–0·905 | — | — | — | — | — | 121–136 | — | — | 67–85 | 37–42 |
| | 100 | 0·827 | | | | | | | | | | |
| **VEGETABLE WAXES** | | | | | | | | | | | | |
| Candelilla wax (*Euphorbia antisyphilitica*) | 15 | 0·950–0·993 | 67–92 | 64–75 | — | — | 10–21 | 47–65 | 34–53 | — | 12–20 | 65–77 |
| Carnauba wax (*Coripha cerifera* L.) | 15 | 0·990–1·000 (0·995) | 83–86 (85) | 80 | 40 | 65–69 | 4–8 (4–5) | 79–95 (79–80) | 75–80 (75–76) | 18–19 | 7–13 (10) | — |
| | 100 | 0·842 | | | | | | | | | | |
| Ocuba wax (from the fruit of *Myristica okuba*) | 15 | 0·920 | 40 | — | — | — | — | — | — | — | — | — |
| Palm wax (*Ceroxylon andicola*) | 15 | 0·992–0·995 | 102–105 | — | — | — | — | — | — | — | — | — |
| Pisang wax (*Musa spec.*) | 15 | 0·965–0·970 | 79–81 | — | — | — | 2–3 | 109 | — | — | — | — |
| Raphia wax (*Raphia Ruffia*) | 15 | 0·950 | 80–82 | — | — | — | — | — | — | — | — | — |
| Rhimba wax | — | — | 60 | — | — | — | — | — | — | — | — | — |

[1] The numbers in brackets indicate the more common limits and mean values.

The purity of a spermaceti is judged from its melting point, acid and saponification numbers and the amount of unsaponifiable matter (*see* General Methods, 4, 7, 8 and 19). Addition of stearine or wax gives an acid number, while that of tallow or other fat increases the saponification number ; solid paraffin or ceresine lowers the saponification number and increases the amount of unsaponifiable matter.

The two following tests are prescribed by the Official Italian Pharmacopœia :

1. SOLUBILITY IN BENZENE. 1 gram of the spermaceti is dissolved in 3 grams of benzene at a gentle heat : on cooling the liquid should remain clear.

2. TEST FOR STEARIC ACID. 1 gram is boiled with 50 c.c. of 90% alcohol and 1 gram of dry sodium carbonate, and filtered : the filtrate, when acidified with a dilute acid, should become barely opalescent, any precipitate indicating the presence of stearic acid.

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According to the Official Italian Pharmacopœia, pure spermaceti should have no odour of fish, should have a specific gravity 0·940–0·950, and should melt at 50–54° or, if recrystallised from alcohol, at 54–55° ; the alcoholic solution should not have an acid reaction ; tests 1 and 2 should be fulfilled.

## SPERMACETI OIL

This is the liquid part of the oil contained in the cephalic cavity of the cachalot and allied species.

The ordinary refined spermaceti oil of commerce is an almost colourless or pale yellow liquid, mobile and nearly odourless.

It is a liquid wax, consisting mostly of esters of one or more higher alcohols with fatty acids of the oleic acid series (fisetoleic acid). It contains 37–45% of higher alcohols (unsaponifiable substances) and about 60% of fatty acids combined with these alcohols ; it contains also very small quantities (0·1–0·4%) of free acids and it turns rancid with great difficulty. Its characters are shown in Table XLIX.

**Detection of Adulterations.**—Adulteration with mineral oils or fatty oils is common. These may be detected by determining the specific gravity, saponification and iodine numbers, and unsaponifiable substances, bearing in mind the following :

1. MINERAL OILS. These lower the saponification number and increase the content in unsaponifiable substances. If the latter are boiled with acetic anhydride and then cooled, the mineral oils separate almost completely from the liquid (*see* General Methods, 19).

2. FATTY OILS. These raise the specific gravity and the saponification number and diminish the proportion of unsaponifiable substances. They may be recognised by the presence of glycerine as indicated under Beeswax, 10.

## CHAPTER X

# INDUSTRIAL PRODUCTS

## FROM THE TREATMENT OF FATTY MATTERS

The most important industrial products obtained from the treatment of fatty matters are: boiled linseed oil, oxidised oils, hardened or hydrogenised oils, Turkey-red oils, oleine, stearine, candles, soap and glycerine.

The methods of analysis used for these materials are largely those employed with fatty substances, being based mainly on the determinations of the various characters (specific gravity, melting point, acid number, saponification number, iodine number, etc.), for which the general methods of the preceding chapter are used. Any special tests necessary are described, as occasion offers, in the following articles.

## BOILED LINSEED OIL

Boiled linseed oil is fluid but more viscous than the crude oil, and is more or less brownish-yellow or brown and of a peculiar odour; there is also a very thick, almost pasty form, which is brown with a greenish fluorescence and has a very marked odour.

In general, the boiled oil is distinguished from the ordinary or crude form by the appearance, the smell, the high specific gravity (0·937–0·99), the presence of drying agents (these are sometimes absent, in which case the distinction is readily made by other characters) and especially by the ease with which it dries.

Boiled linseed oil may be found mixed or adulterated with resin, resin oil, mineral oil, fish or blubber oil, or vegetable oil (colza, soja bean, etc.). Its analysis includes the following determinations and tests:

**1. Specific Gravity, Iodine Number, Saponification Number, Acid Number.**—By the general methods given in the preceding chapter.

**2. Detection of Extraneous Oils.**—As in ordinary linseed oil (*see* p. 404).

**3. Detection of Unsaponifiable Substances and Volatile Oils.**—A few grams of the oil are saponified with alcoholic potash in the usual way and then diluted with 2–3 vols. of water: if the oil is pure the solution is clear or contains a few flocks of lead or manganese hydroxide if dryers are present, but a turbid liquid is obtained if the oil contains mineral or resin oils.

If the oil is distilled in a current of steam, the distillate will contain any oil of turpentine or benzine present.

The unsaponifiable substances may be determined quantitatively by the methods described on p. 388.

**4. Detection of Resin.**—The oil is shaken with an equal volume of about 70% alcohol, the alcoholic liquid being then separated and evaporated, and the residue tested by means of Morawski's reaction (*see* p. 390).

Oils boiled with resinates naturally contain small quantities of resin due to the dryer. Addition of resin should be assumed only when the alcoholic extract is large in amount and the acid number of the oil is high (at least above 12 ; *see* later).

**5. Detection of Siccatives.**—This may be made on the ash of the oil or by dissolving the oil in ether and shaking with dilute nitric acid, the nitric acid solution being tested by the ordinary methods for lead, manganese, calcium, zinc and cobalt.

**6. Drying Properties.**—A drop of the oil is spread uniformly on a glass plate (5 × 10 cm.) and left in the air, protected from direct sunlight, at 15–20°. From time to time the course of the drying is tested by pressing the oily layer hard with the finger : drying is complete when the finger no longer adheres to the surface. The latter is then heated to 100° to see if cracking occurs.

Further, 25 parts of the oil are mixed intimately with 20 parts of zinc white or minium, the paste thus obtained being spread uniformly on an iron plate and left to dry as before.

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Good boiled linseed oil should satisfy the following requirements :

That boiled at a moderate temperature should be only slightly coloured and should yield a perfectly white paste when mixed with pure lead or zinc white.

Its specific gravity should not be below 0·935 and as a rule lies between 0·935 and 0·948, but oil heated at a very high temperature (double boiled, burned) may have a value as high as 0·99. The presence of extraneous oils (vegetable, animal, mineral) lowers the specific gravity.

The *iodine number* may vary from 150 to 172 in light boiled oils, but may fall to 70°, with those strongly boiled and dense.

The *saponification number* should lie between 190 and 195, and is lowered by colza oil and especially by mineral or resin oil.

The *acid number* should not exceed 12 (usually it stands between 7 and 10) and is raised by free resin.

It should not contain *foreign oils* or free *resin*.

The content of *unsaponifiable substances* should not exceed 2% at the most.

The amount of *dryer* should be such that the oil does not leave more than 1% of ash.

In the *drying test*, pale oils should dry completely within 20 hours and dark ones within 12 hours. After being heated at 100°, the dry layer should not exhibit cracking and should become detached in scales when scraped with a knife. When mixed with zinc white or minium, it should dry completely within 24 hours.

## OXIDISED OILS

### (Blown Oils)

These are obtained by passing a current of air through a fatty oil at a temperature of about 70–120° until the oil becomes thick and viscous like castor-oil. Colza, cottonseed, maize, foot and fish oils are usually employed for this purpose.

In general, blown oils are dense, viscous, reddish-brown liquids with a special odour (of boiled oil). In comparison with the corresponding original oils, they have high specific gravities, refractivities and saponification numbers and low iodine numbers (*see* Table, p. 446). Further, they contain marked quantities of hydroxy-acids, and it is characteristic of them that they furnish deep brown fatty acids (almost black with blown fish oils), only partially soluble in ether.

Analysis of these products is concerned principally with the two following cases :

**1. Origin of the Blown Oil.**—It is somewhat difficult to state the nature of the original oil from which a blown oil is prepared, since the specific colour reactions no longer hold. An approximate orientation may be obtained by means of the following criteria.

The fatty acids of oxidised *colza* oil are liquid and their lead salts are mostly soluble in ether.

The fatty acids of oxidised *cottonseed* oil are solid and their lead salts partially soluble in ether.

The fatty acids of oxidised *fish* oils are blackish and saponification of these oils yields a black, pitchy substance insoluble in potash, alcohol or ether and similar to the linoxyn of linseed oil. This does not occur with blown vegetable or foot oils. Blown fish oils are the ones showing the greatest density accompanied by the highest iodine number.

Oxidised *foot* oils exhibit a specific gravity equal to that of oxidised vegetable oils but a less iodine number.

**2. Mixtures of Blown Oils with Mineral Oils.**—Mixtures of heavy mineral oil and oxidised oil (about 5–30%) form good lubricants for marine engines.

Such products are recognisable by the smell and by the following test : 10 grams of the oil are saponified with 25 c.c. of alcoholic potash in the usual way, heating for half an hour on the water-bath in a reflux apparatus with frequent shaking. Without evaporating the alcohol, the whole is transferred to a separating funnel, diluted with 150 c.c. of water, shaken gently and carefully and left to stand until sharp separation into two layers takes place, the lower aqueous layer being then run off and the supernatant mineral oil collected separately (with the help of a little ether), dried and weighed.

On the other hand, the aqueous liquid is acidified and the fatty acids separated : these should exhibit the characters of the acids of oxidised oils, that is, they should be brown and not completely soluble in ether (*see* above).

Examples of the characters of blown oils in comparison with those of the corresponding original oils, are as follows:

| | | Specific gravity at 15°. | Zeiss butyro-refracto-meter Number at 15°. | Saponifi-cation Number. | Iodine Number. | Hydroxy-acids insoluble in petroleum ether, %. |
|---|---|---|---|---|---|---|
| Colza oil | ordinary . | 0·912–0·917 | 68–69 | 170–181 | 94–106 | 0 |
| | blown . . | 0·967–0·977 | 80 | 197–268 | 46–65 | 20–28 |
| Cottonseed oil | ordinary . | 0·922–0·925 | 68 | 191–198 | 107–110 | 0 |
| | blown . . | 0·972–0·979 | 80–81 | 213–226 | 50–66 | 26–29 |
| Ox-foot oil | ordinary . | 0·921 | 62 | 194 | 71 | — |
| | blown . . | 0·972 | 73–74 | 241–242 | 33 | — |
| Fish oil | ordinary . | 0·925 | 78 | 190–191 | 134 | — |
| | blown . . | 0·980–0·985 | 90–91 | 247–248 | 73–74 | — |

## HARDENED OR HYDROGENISED OILS

These are obtained by subjecting liquid fatty oils, either vegetable or animal, to the action of hydrogen at a temperature of 130-140° in presence of a catalytic substance, usually finely divided reduced nickel, or palladium, platinum and various metallic oxides. The unsaturated liquid fatty acids (oleic, linoleic, etc.) of the glycerides of the oils are transformed into solid stearic acid, so that the oils themselves become solid.

These products, marketed under the names of *Talgol, Candelite, Coryphol,* are usually obtained by hydrogenising marine animal oils (in particular, whale oil), but they may also be prepared from vegetable oils (cottonseed, soja-bean, castor, etc.).

As a rule, hardened fats are solid and of the consistency of tallow (with very prolonged hydrogenation they acquire the hardness of waxes) and they have persistent colours, odours and tastes which are similar to those of tallow but no longer recall the original oils. They usually melt at 40-50°, but the strongly hydrogenised ones have still higher melting points. Their fatty acids melt at temperatures 2-3° below the points of fusion of the neutral fats. Their acid number is small and their saponification number normal (190-195), while the iodine number depends on the degree of hydrogenation and may fall to a few units.

Hydrogenised oils give the general colour reactions of the original oils very similarly to the latter: thus, they give Hauchecorne's, Heydenreich's and Bellier's reactions if they are derived from vegetable oils and Tortelli and Jaffe's reaction if from marine animal oils. They do not, however give Halphen's octabromide reaction for marine animal oils (*see* p. 428) or Halphen and Milliau's reactions for cottonseed oil; but partially hydrogenised cottonseed oil, even when solid, still gives Halphen's reaction quite distinctly.

Hydrogenised oils contain unchanged the unsaponifiable substances

(phytosterol or cholesterol) of the original oils and, as a rule, traces of the catalyst (mostly nickel) are found.

The analysis of these products includes :

**1. Characters and Origin.**—Of the characters of hardened oils, those of special importance, besides the objective ones, are the melting point, solidifying point of the fatty acids (titer) and the acid, saponification and iodine numbers.

To ascertain the origin of a hardened oil, the unsaponifiable substances (sterols) must be extracted and identified (*see* Hog's Fat) : hardened animal oils contain cholesterol and the vegetable ones, phytosterol.

The Tortelli and Jaffe reaction (*see* p. 430) indicates if a hardened oil is prepared from a marine animal oil.

**2. Test for Traces of Catalyst** (*Nickel*).—This may be made on the ash of the product or, according to Fortini, in the following way :

5 to 10 grams of the fat are heated for half an hour on the water-bath with as much conc. hydrochloric acid, with frequent, vigorous shaking ; the acid is then filtered through a moist filter into a dish, evaporated to dryness, and the residue moistened with a few drops of 1% alcoholic dimethyglyoxime solution : in presence of nickel a red coloration is obtained, this being rendered more evident when the solution is made slightly alkaline with a drop of dilute ammonia.

If the extract of the acid is highly coloured it is well to redissolve it in a little water and decolorise with animal charcoal.

## TURKEY-RED OIL

This is obtained by treating castor oil with sulphuric acid, eliminating the excess of acid by washing with water and sodium sulphate solution and then neutralising more or less completely with ammonia or soda. It consists, therefore, essentially of *ammonium* or *sodium sulphoricinate.* It is a clear, yellow liquid with the odour of castor oil. It dissolves in a small quantity of water but further addition of water (10 vols. per 1 vol. of the oil) yields a perfect, white emulsion which persists for some hours and is faintly acid to litmus paper. Sulphoricinates neutralised with ammonia or soda dissolve, however, in water in all proportions, but faint acidification of the solution with a few drops of acetic acid results in emulsification. If an excess of acid or sodium chloride is added, either to the emulsion or to the solution of a sulphoricinate, an oily layer separates.

Sulphoricinates are also completely dissolved by ammonia, the solution not being rendered turbid by dilution with water. Alcohol, too, completely dissolves them.

Ammonium sulphoricinate gives ammonia when heated with sodium hydroxide, while sodium sulphoricinate is incinerated and the ash examined for soda.

Genuine Turkey-red oil is sometimes replaced by analogous preparations with bases of sulphonated olive, arachis, cottonseed or resin oil or oleic acid and is often adulterated with mineral oil.

It is also to be borne in mind that certain emulsive lubricating oils,

dealt with in the chapter on mineral oils (*see* p. 368), have a basis of sulphoricinate or sulpholeate.

Analysis of Turkey-red oil comprises the following determinations and tests, the second and fifth being of special importance for the evaluation of the product.

**1. Solubility and Emulsivity.**—2 or 3 c.c. of the oil and as much water should give complete solution and addition of about 10 vols. of water should then yield a persistent homogeneous emulsion of a faintly acid reaction.

Dilute ammonia should also dissolve the oil completely and the solution should remain clear on dilution with a large quantity of water.

**2. Total Fat.**—10 grams of the oil are heated somewhat in a conical flask with 50 c.c. of water, 25 c.c. of dilute hydrochloric acid (1 : 5) being added and the liquid boiled for 3-5 minutes (until the fused fat becomes clear), allowed to cool, transferred to a separating funnel, into which the flask is washed with a little water and with 200 c.c. of ether. The whole is vigorously shaken and allowed to stand, the acid aqueous liquid being removed and the ethereal solution washed with three successive quantities of 15 c.c. of water, these wash waters being added to the aqueous acid liquor and this kept for the determination of the sulphuric acid (*see* 3, below). The bulk of the ether is distilled from the ethereal solution in a conical flask and the residue transferred to a tared beaker; when the remainder of the ether has evaporated, the residual mass is dried for 1–2 minutes over a naked flame (a medium flame being passed under the beaker until the fat ceases to froth) and then for half an hour in an oven at 105° and weighed. The weight of fat thus found, multiplied by 10, gives the percentage of total fat in the oil.

The fat may then be used for investigating the nature of the oil as in 5 (below).

**3. Determination of the Sulphuric Acid.**—The aqueous liquid obtained as above is precipitated with barium chloride, the weight of barium sulphate thus precipitated corresponding with the *total sulphuric acid* ($SO_3$) in the oil.

On the other hand the *sulphuric acid as ammonium or sodium sulphate* is determined by treating 10 grams of the oil with saturated sodium chloride solution (quite free from sulphate), filtering through a moist filter, washing well with the saturated sodium chloride solution, diluting the filtrate and precipitating the sulphate in it with barium chloride.

Subtraction of the percentage of $SO_3$ as ammonium or sodium sulphate from the total percentage gives the *sulphuric acid* (as $SO_3$) as *sulphoricinate* and this, multiplied by 4·725, gives the percentage of *sulphoricinoleic acid* in the oil.

**4. Neutral Fat.**—30 grams of the oil are dissolved (in a separating funnel) in 50 c.c. of water, 20 c.c. of ammonia solution and 30 c.c. of glycerine. The whole is shaken with two successive quantities of 100 c.c. of ether and the united ethereal solutions washed several times with water and then distilled, the residue being dried at 100° and weighed. This weight, multiplied by $\frac{100}{30}$, gives the percentage of neutral fat in the oil.

**5. Nature of the Oil.**—To ascertain if a Turkey-red oil has been prepared from castor oil or from other oil, or adulterated with mineral oil, the total fat obtained by method 2 (above) is examined.

On this fat the iodine and acetyl numbers are first determined: an iodine number above 70 and an acetyl number below 140 show immediately that the oil has not been obtained from pure castor oil. The specific colour reactions of the different oils (cottonseed, sesamé, etc.) may then be tried.

It is also to be borne in mind that the emulsive oils prepared with olive, cottonseed, colza, sesamé and similar oils do not usually give clear solutions with alcohol, as does pure emulsive castor oil.

For detecting mineral or resin oils the saponification test is made.

**6. Ammonia or Soda.**—From 7 to 10 grams of the oil are dissolved in a little ether and the solution extracted four successive times with dilute sulphuric acid (1 part of conc. acid and 6 parts of water). The acid liquids are then distilled with excess of caustic soda—when ammonium sulphoricinate is concerned—and the ammonia absorbed in standard acid; with sodium sulphoricinate, the acid liquors are evaporated to dryness and the soda weighed as sulphate.

**7. Iron.**—The oil is shaken with dilute sulphuric acid and a few drops of potassium ferrocyanide solution, ether being then added and the liquid again shaken and then left to stand. If iron is present, a more or less intense blue ring appears at the zone of contact of the two liquids.

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Good Turkey-red oils, prepared from castor oil, usually contain 45–60% of total fatty substance (the rest being water), but there are more concentrated types with 85–90% of fat (double oils). Those with about 45% of fat have the specific gravity 1·017–1·035 at 15°. The greater part of the fat consists of insoluble sulpho-acids and a small part of soluble sulpho-acids; neutral fat is present only in small proportion (1–2%). No iron should be present.

## OLEINE

### (Oleic Acid)

This consists of the liquid fatty acids (mainly oleic acid)—more or less completely separated from the solid acids—yielded by animal tallow, bone fat, vegetable tallow, palm oil and other fats. According to its method of preparation, it is distinguished as *olcine of saponification* and *distillation oleine* (the latter, unlike the former, usually contains a large proportion of hydrocarbons resulting from the method of its preparation). In either case it is a brownish-yellow or brownish-red liquid, with a peculiar odour, easily soluble in 85% alcohol, acetic acid or petroleum ether.

The most important determination to be made in commercial oleines are the following:

**1. Acid, Saponification, Ester and Iodine Numbers.**—These are determined by the ordinary methods already described in the preceding chapter. The ester number, divided by 2, gives the content of neutral fat. The percentage of free acids (calculated as oleic acid) is usually called the grade or titer of the oleine.

**2. Unsaponifiable Substances.**—A preliminary test for these substances is as follows: 6–8 drops of the oleine and 5 c.c. of seminormal alcoholic potash are boiled for two minutes in a test-tube and then diluted with 15 c.c. of water: in this way pure oleine yields a clear or almost imperceptibly milky liquid (distillation oleine), whereas a turbid liquid is obtained with oleine mixed with mineral oil.

To separate and estimate the unsaponifiable substances, the methods indicated on p. 388 are used.

To ascertain if the unsaponifiable matter is composed of the hydrocarbons naturally occurring in distillation oleine or of added mineral oil, the rotatory power and the iodine number of the unsaponifiable matter are determined: in the former case the value of $[\alpha]_D$ is from + 4·8° to + 9·6° and the iodine number 62–69, whereas mineral oils have practically no rotatory power or iodine number.

**3. Determination of the Solid Fatty Acids (Palmitic and Stearic).**—This may be effected by the methods indicated in the preceding chapter (p. 384) or by determining the *solidifying point of the oleine* (*see* preceding chapter, p. 418). From the point of solidification obtained, the content of stearine is deduced by means of de Schepper and Geitel's table, which has been prepared with the aid of mixtures of pure oleine with solidifying point 5·4° and stearine with solidifying point 48°:

TABLE L

**Content of Stearine in Oleine**

| Solidifying Point (° C.). | Percentage of Stearine (48°). | Solidifying Point (° C.). | Percentage of Stearine (48°). | Solidifying Point (° C.). | Percentage of Stearine (48°). |
|---|---|---|---|---|---|
| 6 | 0·3 | 15 | 6·6 | 23 | 15·7 |
| 7 | 0·8 | 16 | 7·7 | 24 | 17·0 |
| 8 | 1·2 | 17 | 8·8 | 25 | 18·5 |
| 9 | 1·7 | 18 | 9·8 | 26 | 20·0 |
| 10 | 2·5 | 19 | 11·2 | 27 | 21·7 |
| 11 | 3·2 | 20 | 12·1 | 28 | 23·3 |
| 12 | 3·8 | 21 | 13·2 | 29 | 25·2 |
| 13 | 4·7 | 22 | 14·5 | 30 | 27·2 |
| 14 | 5·6 | | | | |

***

A good oleine should have an acid number about 179, corresponding with about 90% of free fatty acids, calculated as oleic acid. Oleines are however found with 80–98% of free acids.

The content of neutral fat may vary from 0 to 20% (usually 10–15%).

The iodine number is usually 80–90. If it exceeds 90, the presence of linoleic, linolenic and other less saturated acids derived from drying vegetable oils is indicated.

The unsaponifiable substances should not exceed 2% in saponification oleine, but may reach 10% in distillation oleine.

In saponification oleine, up to 20% of neutral fat and up to 2% of unsaponifiable matter are permitted, and in distillation oleine, up to 5% of neutral fat.

## WOOL FAT OLEINE

This is the liquid part of distilled wool fat, consisting of free fatty acids (40-60%), hydrocarbons and a little cholesterol and isocholesterol.

It is a more or less turbid liquid of a reddish-brown colour and more or less fluorescent and with a peculiar odour recalling that of wool fat. It is soluble in 95% alcohol, ether, benzine, etc.

With conc. sulphuric acid, its chloroform solution gives a red coloration with a green fluorescence (cholesterol). It may be adulterated with mineral or resin oils or resin.

Its analysis includes the following:

**1. Acid and Saponification Numbers and Unsaponifiable Matter.**—Use is made of the methods described in the preceding chapter (General Methods, 7 and 19).

**2. Mineral and Resin Oils.**—From 50 grams or more of the oleine the unsaponifiable substances are extracted by the ordinary methods, and their specific gravity, index of refraction, rotatory power (in about 3–4% benzene solution and in a tube 10 cm. long at a temperature of 18–20°) and iodine number determined.

The presence of mineral oil may be presumed when these unsaponifiable substances have very low rotatory power and iodine number. The presence of resin oil may be recognised by the specific gravity being greater than 0·917 and the refractive index above 1·51.

**3. Resin.**—The soap solution remaining after the separation of the unsaponifiable matter is decomposed with an acid and the fatty acids then tested by means of Morawski's reaction (*see* preceding chapter: General Methods, 20).

For its quantitative determination Twitchell's method (*ibid.*) is followed.

Before applying Morawski's reaction, it is necessary thoroughly to separate the unsaponifiable matter in order to remove the cholesterol, which gives a similar reaction.

***

Pure wool fat oleine should not contain more than 60% of unsaponifiable substances. These are liquid and have approximately the appearance of mineral oils; they should, however, have: D = 0·900–0·917; refractive index (at 18–20°) = 1·49–1·51; $[\alpha]_D = +15°$ at least (in exceptional cases as low as 10°) and iodine number = 50–80.

## STEARINE

### (Stearic Acid)

This is a mixture of solid fatty acids (stearic and palmitic)—more or less completely separated from the liquid acids—obtained from animal tallow or from some vegetable fat and used especially in the manufacture of candles.

According to their methods of manufacture, they are distinguished as *stearine of saponification* and *distillation stearine*, the latter containing, unlike the former, iso-oleic acid and stearolactone.

In general stearine forms hard, opaque, white masses, somewhat greasy to the feel and soluble in alcohol, especially in the hot.

Analysis of commercial stearines comprises principally the following:

**1. Solidifying Point (Titer).**—This is determined by Dalican's method (*see* p. 418), the content of stearine being deduced by means of the corresponding table; when, however, fatty acids alone are concerned, the number given in the table is multiplied by $\frac{100}{95}$ (*see* p. 419).

**2. Acid, Saponification and Iodine Numbers.**—By the methods given in the preceding chapter.

The iodine number depends on the quantity of oleic acid (and maybe of iso-oleic acid) in the stearine and this may be calculated from the iodine number by means of the formula

$$O = \frac{100}{90,} \times I, \text{ or } O = 1{\cdot}11 \times I,$$

where O = oleic acid sought I = iodine number of the stearine and 90 is the iodine number of pure oleic acid.

**3. Detection of Various Extraneous Substances.**—Commercial stearines sometimes contain solid paraffin or ceresine, wool fat stearine, wax and carnauba wax. The presence of such substances may be suspected as a rule when the acid number of the stearine is less than 195, but may be proved definitely as follows:

(*a*) A few grams of the stearine are digested in the hot with 95% alcohol. If the substance does not dissolve completely, the liquid is allowed to cool and filtered and an examination made of the insoluble part. The latter may contain solid paraffin or ceresine, beeswax or carnauba wax, their presence being indicated by the melting point, the acid and saponification numbers, etc. (*see* articles on Paraffin Wax, Ceresine and Beeswax).[1]

(*b*) A quantity of the stearine is hydrolysed with alcoholic potash and the unsaponifiable substances extracted and examined by the methods indicated on p. 388 *et seq.*; the presence of cholesterol will indicate the presence of wool fat stearine in the substance.

If then it is necessary to determine the various acids composing a stearine (stearic, palmitic, oleic) and to test for stearolactone, the methods indicated in the preceding chapter (*see* pp. 384 and 383) may be followed.

Finally, when the presence of lactones is excluded, that of neutral fat may be deduced from the ester number and may be confirmed by testing for glycerine (*see* p. 384).

***

Commercial stearines usually solidify between 48 and 55° (*titer*), the value for saponification stearine being somewhat higher than that for distillation stearine.

The *acid number* should not be less than 195: if it is less than this, the presence of neutral fats or extraneous substances is denoted.

[1] The presence of carnauba wax may be recognised also from the fact that, besides lowering the acid and saponification numbers of the stearine, it raises the melting point considerably, 5% of carnauba wax being sufficient to raise the melting point of a stearine by 10°.

The *saponification number* is equal or almost equal to the acid number with saponified stearine and somewhat greater with distillation stearine.

The *iodine number* is barely a few units in good saponification stearines, but may reach 15–30 in distillation stearines, owing to the presence of iso-oleic acid.

## WOOL FAT STEARINE

This is the solid part of distilled wool fat and consists of fatty acids and unsaponifiable substances (hydrocarbons, cholesterol).

According to the consistency, it is distinguished as *Soft stearine*, melting below 45°, and *Hard stearine* or *Wool fat wax*, melting above 45°.

In general, these products have a waxy appearance, a yellow or brownish colour and a pronounced odour of wool fat, and they are soluble in hot alcohol and in ether, benzene or chloroform. When treated with conc. sulphuric acid, the chloroform solution turns red and afterwards violet with a green fluorescence (cholesterol).

Analysis of wool fat stearine includes determinations of the melting point, acid number and content of unsaponifiable substances, as well as tests for added hydrocarbons (vaseline, paraffin wax) or resin.

**1. Vaseline or Paraffin Wax.**—The unsaponifiable substances from 50 grams of the stearine are boiled for 2 hours in a reflux apparatus with double their weight of acetic anhydride. The product is then washed repeatedly with boiling water until the reaction is neutral and in one part the acetyl number is determined (*see* p. 378). Another part (about 5 grams) is boiled with 50 c.c. of 90% alcohol, the liquid being filtered off and the residue boiled with 40 c.c. and then with 30 c.c. of 90% alcohol. Of the part insoluble in alcohol, which consists of hydrocarbons alone, the specific gravity, rotatory power (in benzene solution at about 20°) and iodine number are determined.

**2. Resin.**—This is tested for as in wool fat oleine (*see* p. 451).

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According to Marcusson and Skopnik [1] and to Coen,[2] wool fat stearines may melt between 40° and 65°; they contain 56–90% of free acids (calculated as stearic acid) and 9–42% of unsaponifiable substances, which are brown, fluorescent, pasty or semi-liquid masses with a faint aromatic odour and have the acetyl number about 25–37, the $[\alpha]_D$ + 12° to + 30° and the iodine number 47–74.

The portion of the unsaponifiable matter which does not combine with acetic anhydride (hydrocarbons free from higher alcohols) has D = 0·907–0·936, $[\alpha]_D$ = + 12° to + 21°, and iodine number = 26–54.

Addition of extraneous hydrocarbons may be suspected when the acetyl number of the unsaponifiable substances is less than 25 and the portion of them not combinable with acetic anhydride has a specific gravity less than 0·9, $[\alpha]_D$ less than + 12° and an iodine number less than 26.

[1] *Zeitschr. angew. Chem.*, 1912, p. 2577.

[2] *Annali del Lab. chim. centrale delle Gabelle*, Vol. VI, p. 567.

## DÉGRAS

Genuine dégras (*natural dégras*) is a secondary product of the chamoising of skins. It consists of marine animal oil (especially whale oil), in which the action of atmospheric oxygen has led to the formation of resinous hydroxy-acids (*Dégragène*), emulsified with water and containing small proportions of mineral substances (soda, lime, sulphates) and organic residues (hide, membranous fragments) resulting from the method of preparation.

This product forms a fairly dense, almost pasty, yellow or orange liquid, which has a special odour recalling that of fish oil and remains homogeneous even on long standing.

*Artificial dégras* is obtained by mixing natural dégras with fish, mineral or resin oil, vaseline, wool fat, tallow, etc., or by artificial oxidation of fish oils, followed by emulsification with water and sometimes by addition of the other extraneous substances mentioned above.

Artificial dégras is also a yellow or orange dense liquid, which is usually more liquid than the natural product and has a peculiar fish oil odour; on long standing, it tends to divide into two layers, the water settling to the bottom.

Analysis of dégras includes various determinations and tests to serve as a guide in ascertaining if it is a natural or artificial product, if it is pure, that is, based solely on fish oils, or if it is mixed with tallow, wool fat, mineral oils, vaseline or resin oils, these being the most frequent additions to dégras.

The principal determinations are as follows:

**1. Water.**—10 grams of the dégras are placed in a porcelain dish previously heated to redness with about 10 grams of coarse quartz sand and tared; the fat is mixed well with the sand and the dish and contents dried at 120° until of constant weight (4–5 hours). The loss in weight gives the water.

**2. Non-fatty Substances (Organic Residues).**—20 grams of the dégras are dried in an oven at 120° or even over a direct flame, the liquid being stirred with a thermometer and care taken that its temperature does not exceed 105°; the dried product is dissolved in petroleum ether and the solution filtered through a tared filter, the insoluble matter being washed with petroleum ether and then with a little ether or benzene and alcohol, dried at 100° and weighed.

This insoluble matter consists principally of epidermis and hide residues readily recognisable with a lens or microscope, together with a few other impurities.

On the other hand, evaporation of the petroleum solution and weighing of the residue dried at 105° gives the total fat; the latter is used for the determinations indicated under 4 (below).

**3. Ash.**—10 grams of the dégras are carefully heated in a platinum dish over a naked flame until copious fumes are emitted, the dish being then heated more strongly on a sand-bath and finally in a muffle at a dull red heat. The ash is mainly alkali and alkaline-earthy sulphates; it is

well to test it for oxide of iron, which should be present barely in traces, since dégras containing iron spots the leather.

**4. Acid and Saponification Numbers.**—These are determined in the usual way on the dry fat from the determination of the non-fatty substances (2). From the acid number the percentage of free acids expressed as oleic acid (*see* p. 374) is calculated.

**5. Dégragene.**—This is the special resinous substance formed by the oxidation of the fish or blubber oils [1] and is what gives *body* to the dégras, increases its power of emulsivity with water and renders it specially adapted to the treatment of skins. It is determined as follows [2]:

10 grams of the dégras, either as it stands or after drying at 100° as indicated under 2 (above), are dissolved together with 7 grams of caustic soda in 10 c.c. of water and 50 c.c. of alcohol, the solution being heated on a water-bath in a reflux apparatus until saponification is complete (about 2 hours). The alcohol is then expelled, the soap dissolved in water and acidified with hydrochloric acid, and the whole boiled until the mixture of fatty acids and dégragène becomes quite fluid. When cool, the mass is transferred to a separating funnel and the flask rinsed out with about 150 c.c. of petroleum ether boiling below 75°; the whole is well shaken and allowed to stand until the aqueous acid liquid separates sharply from the petroleum solution, the former being then run off. The funnel then contains the petroleum ether solution of the fatty acids and of the unsaponifiable substances of the dégras, together with an insoluble, blackish, resinous solid constituting the dégragène, which adheres well to the walls of the funnel, so that the petroleum solution may be poured from the top of the funnel without any of the dégragène being lost. The dégragène is then washed with a little petroleum ether and dissolved in hot alcohol, the solution being filtered if necessary, the alcohol evaporated and the residue dried at 100–105° and weighed.

**6. Unsaponifiable Substances.**—According to Baldracco,[3] these may be determined exactly as follows: 15–20 grams of the dégras are saponified by boiling with 5 grams of caustic potash dissolved in 10 c.c. of water and 50 c.c. of alcohol for 2–2½ hours in a reflux apparatus, the liquid being then transferred to a dish and the alcohol completely expelled by evaporation on a water-bath. The residue is well mixed with 8 grams of sodium bicarbonate and 50–60 grams of coarse quartz sand previously washed and calcined, and completely dried in an oven at 110°. The mass is then broken into small pieces, placed in an extraction thimble and extracted with petroleum ether boiling below 75°.

The petroleum solution is washed several times with water in a separating funnel and then evaporated, the residue, when dried at 110° and weighed, representing the unsaponifiable matter contained in the dégras.

[1] The largest proportions of dégragène are furnished by whale oil and cod-liver oil, which yield, therefore, the best dégras.

[2] This is the method proposed by the Committee for the analysis of dégras at the Seventh Congress of the International Association of Leather Trade Chemists, Turin, 1904.

The other determinations are also those suggested by this Committee.

[3] *See* preceding note.

This residue may then be tested for cholesterol and for mineral and resin oils in the way indicated on p. 388, in order to ascertain if the dégras contains wool fat, mineral oils and other unsaponifiable matters.

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Good dégras is golden-yellow or orange and homogeneous and keeps well.

Natural dégras usually contains 15–25% of *water*, while the artificial products contain 10–25%.

The other components may vary within the following limits, which are *referred to the dry dégras* (free from water):

The *non-fats* (various organic residues) may reach 8% in natural dégras (ordinarily 2–5%), but are less than 1% in artificial dégras.

The *ash* may amount to 5% with natural dégras, but is less than 1% in the artificial product; it should contain only traces of iron (not more than 0·05% of the original dégras).

The *free fatty acids*, calculated as oleic acid, may vary from 20 to 30% in natural dégras, but are usually less than 20% in the artificial ones.

The *saponification number* is above 200 (220–240) in natural dégras and not less than 190 in artificial dégras. A value less than 190 (referred to the dry substance) denotes the presence of extraneous matter, such as mineral or resin oils, vaseline or wool fat.

The proportion of *dégragène* is somewhat variable, since it depends on the mode of preparation of the dégras. Usually natural dégras contains 6–20% and the artificial product not more than 10% of dégragène.

The *unsaponifiable matter* does not exceed 3% in pure dégras, whether natural or artificial, but is considerably higher in products adulterated with mineral or resin oils, vaseline or wool fat.

## CANDLES

Three types of candles are usually sold: stearine, paraffin and wax.

*Stearine candles*, which are opaque and white, should be made from stearine (mixture of stearic and palmitic acids, etc.; *see* Stearine), but very often they contain a certain quantity of paraffin wax (up to 50%) and sometimes ceresine or a small quantity of carnauba wax (to raise the melting point).

*Paraffin candles*, which are translucent and white, are made from paraffin wax with a high melting point (about 50°), usually with the addition of 3–15% or even more (up to about 33%) of stearine, such being *mixed* or *composite candles*.

*Wax candles*, which are yellowish and opaque and possess the characteristic odour of wax, should be made from pure beeswax, but they are nowadays usually made from mixtures of wax, paraffin wax, ceresine and stearine, the wax being present often in small amount.

Analysis of candles is usually made with the object of determining the composition, but includes also tests of the illuminating power and bending properties.

**1. Composition.**—An idea of this is obtained firstly from the objective characters (*see* above). The composition is then determined qualitatively and quantitatively by determinations of the solidifying point, of the acid, saponification and iodine numbers, of the unsaponifiable substances and the nature of the latter, the instructions laid down in the articles on stearine,

paraffin wax, ceresine and beeswax being followed according to the type of candle examined.

For the quantitative determinations it is well to melt a whole candle or at least various pieces taken from several candles at different points in order to obtain a homogeneous and representative sample.

It is further necessary to determine the weight of the *wick*, several pieces being broken from one or more candles and weighed and the wick then carefully separated and weighed: the weight of the wick is referred to 100 parts of candle.

The commonest cases of analysis of candles are the following:

(*a*) MIXED STEARINE AND PARAFFIN (OR CERESINE) CANDLES. About 10 grams of the sample are heated and shaken with 50 c.c. of 90% alcohol on the water-bath, the liquid being subsequently titrated with decinormal potassium hydroxide in presence of phenolphthalein: 1 c.c. N/10-KOH = 0·027 gram of stearine (mean molecular weight of ordinary stearine = 270).

The liquid is then again heated on the water-bath for about an hour, with frequent shaking, with 4–5 c.c. of concentrated potassium hydroxide solution to saponify the small quantity of neutral fat or any lactones present in the stearine (for greater precision the saponification number also may be determined). The solution is then diluted with water and allowed to cool until the paraffin is thoroughly solidified to a *solid disc*, the aqueous liquid being then decanted off and the paraffin washed several times with water, being heated and cooled each time. The washed paraffin is finally collected into a dish, dried in an oven at 105° and weighed.

The paraffin thus separated is then tested for ceresine by the methods given on p. 364.

The stearic acid (stearine) calculated from the acid number and the paraffin weighed directly are then referred to 100 parts of candle, allowance being made for the weight of the wick (*see* example given below for case *b*).

For rapid, approximate determinations it is sufficient to calculate the stearic acid from the acid number and the paraffin by difference.

(*b*) MIXED WAX, STEARINE AND PARAFFIN CANDLES. In these candles it may be necessary to calculate either all three of the components or only the paraffin (or ceresine).

1. *Determination of all of the components.* The acid and saponification numbers are determined in the usual way, the various components being then calculated as in the following example.

EXAMPLE: The wick of a candle is found to represent 0·4% of the weight of the candle, while the wick-free mass has:

Acid number = 77·0
Saponification ,, = 84·7,

so that

Ester number = 7·7.

Assuming the mean ester number of wax to be 75, the mean saponification number of wax to be 95 and the mean saponification number of stearic acid to be 207, the various components are calculated as follows:

(*a*) The wax ($x$) is given by the ester number,

$$75 : 100 :: 7{\cdot}7 : x,$$

consequently,

$$x = 10{\cdot}26\% \text{ of } wax.$$

(*b*) The saponification number (*y*) due to the wax will be given by

$$100 : 95 = 10{\cdot}26 : y,$$

so that

$$y = 9{\cdot}75.$$

This number *y* is deducted from the saponification number found for the substance,

$$84{\cdot}7 - 9{\cdot}75 = 74{\cdot}95,$$

and from this the stearic acid (*z*) is deduced from the proportion,

$$207 : 100 = 74{\cdot}95 : z,$$

so that,

$$z = 36{\cdot}11\% \text{ of } \textit{stearic acid}.$$

(*c*) The solid paraffin is then given by difference,

$$100 - (10{\cdot}26 + 36{\cdot}11) = 53{\cdot}63\% \text{ of } \textit{paraffin}.$$

(*d*) The composition of the entire candle (with the wick) is thus:

| | |
|---|---|
| Wick | 0·40% |
| Wax | 10·22 |
| Stearic acid | 35·96 |
| Paraffin | 53·42 |

2. *Determination of the paraffin (or ceresine) alone.* In this case 10 grams of the candle are boiled for 3–4 hours with alcoholic potash in a flask fitted with a long tube to act as reflux condenser and then left to cool until the paraffin has set well at the surface of the liquid. The latter is then poured off together with all the unsaponifiable matters of the wax which remain suspended in a flocculent form, care being taken that the whole of the paraffin remains in the flask. The paraffin is then again boiled for an hour with alcoholic potash, the whole being afterwards transferred while still hot to a separating funnel, the flask being rinsed out with boiling water so as to obtain all the paraffin in the funnel. The aqueous alcoholic liquid is run away and the paraffin remaining in the funnel washed several times with hot water and subsequently rinsed out into a small beaker with the help of very hot water. After cooling, the solid paraffin disc is dried at 100–105° in a tared dish and weighed.

This paraffin is then tested for ceresine by the methods given under Paraffin wax and Ceresine.

**2. Illuminating Power.**—This is measured as with petroleum (*see* Chapter VIII, Lighting Oil, 7).

**3. Bending Test.**—This test, made especially with paraffin candles, consists in introducing the base of the candle into a suitable support so that the candle is horizontal and leaving it in a room at a constant temperature of 22–25° for some hours to ascertain if it becomes curved and, if so, to what extent. A standard candle is used for purposes of comparison.

## SOAPS

Soaps consist essentially of potassium or sodium salts of fatty acids, potash soaps being soft and the more common soda soaps hard.

Besides these salts, all soaps contain water and, according to their method of manufacture and use: free alkali (hydroxides or carbonates), neutral fat, colophony (as alkali resinates), and various extraneous sub-

stances such as alkali carbonates, chlorides, sulphates, silicates and borates, kaolin, talc, starch, sugars, glycerine, alcohol, etc., essential oils (in scented soaps) or antiseptic and medicinal substances (in medicinal soaps).

The purest soaps are the so-called *curd soaps*, obtained by precipitation with common salt, and those prepared from the free fatty acids. Such soaps are neutral or only slightly alkaline, and this group includes, for instance, toilet soaps in general, so-called Marseilles white soap and certain mottled soaps.

So-called "*cold*" soaps, obtained by saponifying fats with an alkaline lye without adding common salt, are usually very alkaline; they contain the glycerine and all the impurities of the fats and alkali used. Potash soaps belong to this class.

Soaps are analysed to ascertain their composition and to see if they are suited to definite uses. Analysis includes mainly determinations of the water, total fat, alkali, resin, glycerine, etc.

**1. Sampling.**—The various determinations require at least 100 grams of soap, which is stored in a well-dried and closed glass jar.

With soap in small pieces or cakes, these are cut into at least four parts (lengthwise and crosswise), from which thin shavings are taken and cut up finely, the whole being thoroughly mixed and a portion taken for analysis.

With soap in blocks or large rectangular pieces, two triangular prisms with their bases on two opposite sides are taken so as to represent proportionately the dried outer part and the more hydrated inner part; these prisms are rapidly cut up, well mixed and the sample to be analysed then taken.

Soft or powdered soaps are well mixed with a spatula or in a mortar and the sample then taken.

**2. Water.**—In a platinum dish, tared with a glass rod, 5–8 grams of the soap are weighed, the dish being then heated in an oven first at 60–70° and then at 100–105° until of constant weight, the mass being stirred from time to time with the rod. Loss of weight represents water.

For soft soaps or others containing a large proportion of water, a certain amount of siliceous sand or ground pumice, previously ignited, is tared in the dish with the glass rod.[1]

**3. Total Fat.**—20 grams of the soap, dissolved in water, are decomposed by excess of dilute sulphuric acid (1 : 3) or of normal sulphuric acid (*see also* 4), the solution shaken with 100 c.c. of petroleum ether, b.pt. not above 65°, and the acid liquid separated and again shaken with 100 c.c. of petroleum ether. The two petroleum extracts are united, washed with water, filtered (if necessary) into a tared dish and evaporated at a low temperature, the residue being dried in an oven at about 110° to constant weight.

This gives the total fat, which, besides the fatty acids and resin acids constituting normal soap, may contain also neutral fat and unsaponifiable substances; it is therefore examined further (*see* below: 5, 8 and 11).

[1] If the soap contains alcohol, hydrocarbons or other volatile substances, these are vaporised with the water; in such cases the water is determined by difference after the other components of the soap have been determined.

The aqueous acid liquid, separated from the petroleum ether, may be utilised for the determination of the alkalies (*see* 4).

**4. Total Alkalies.**—This determination may be combined with the preceding one of the total fat. For this purpose it is sufficient to decompose the aqueous solution of 20 grams of the soap with 100 c.c.of normal sulphuric acid and then to proceed as in 3, care being taken to lose no trace of the aqueous acid liquid separated from the petroleum ether solution.

This liquid, collected quantitatively in a conical flask, is titrated with normal potassium hydroxide solution in presence of methyl orange.

The difference between the volume of normal acid added to the soap solution and the volume of normal alkali necessary to neutralise the remaining free acid, represents the total alkali—existing as hydroxides, carbonates, silicates, borates and soaps—in the soap. This is expressed as sodium oxide for hard or powdered soap, and as potassium oxide for soft soap; 1 c.c. normal $H_2SO_4 = 0{\cdot}031$ gram of $Na_2O = 0{\cdot}047$ gram of $K_2O$.

**5. Alkalies combined with Fatty Acids.**—The alkalies combined with fatty (or resin) acids, that is, as soaps, are deduced from the acid number of the total fat obtained as in 3.

The acid number is determined as on p. 374, and the results are expressed as $Na_2O$ for hard or powdered soap and as $K_2O$ for soft soap.

**6. Free Alkalies.**—The presence of excess of alkali in a soap is detected (1) by dissolving 1 part of the soap in 50 parts of 95% alcohol and adding a few drops of phenolphthalein solution (red coloration), or (2) by dropping on to a section of the soap, recently cut, a drop of mercuric chloride solution (yellow coloration) or mercurous nitrate solution (black coloration).

Quantitatively free alkalies as hydroxide and as carbonate are determined as follows:

(*a*) ALKALIES AS HYDROXIDE. A solution of 10–15 grams of anhydrous glycerine in 100 c.c. of absolute alcohol is neutralised, if necessary, with a few drops of alcoholic potash (phenolphthalein as indicator). 5 grams of the soap are then dissolved in it and 2–5 c.c. of cold, saturated alcoholic strontium chloride solution added to precipitate the alkali carbonates, the free alkalinity being then titrated with standard alcoholic stearic acid solution in presence of phenolphthalein.[1]

(*b*) ALKALIES AS CARBONATE. If the soap does not contain silicates, borates or other alkaline salts, the alkalies as carbonate may be calculated *indirectly* or *by difference*, by subtracting from the total alkali (*see* 4) the sum of the alkali as hydroxides and that combined with the fatty acids (*see* 5 and 6*a*), all expressed as $Na_2O$ or $K_2O$: this difference, converted into $Na_2CO_3$ or $K_2CO_3$, represents alkalies as carbonates.

When silicates, borates or other alkaline salts are present, the best way to determine the carbonates is to decompose the soap with dilute sulphuric

[1] The alcoholic stearic acid solution is prepared by dissolving about 7 grams of stearic acid in a litre of absolute alcohol (approximately N/40 solution) and the titer, i.e., the number of grams of NaOH or KOH corresponding with 1 c.c., determined by N/10-potassium hydroxide solution in presence of phenolphthalein. With reference to this and other determinations, *see* the paper by G. Gianoli, "On Uniform Methods of Soap Analysis" (*L'Industria*, 1914, p. 488).

acid and absorb the carbon dioxide liberated in caustic potash solution in the ordinary manner.[1]

**7. Free Fatty Acids.**—These are determined only when the soap does not exhibit an alkaline reaction.

20 grams of the soap are dissolved in neutral 60% alcohol and the solution titrated with alcoholic decinormal caustic potash in presence of phenolphthalein. The acidity is expressed as oleic acid : 1 c.c. N/10-KOH = 0·0282 gram of oleic acid.

**8. Neutral Fat and Unsaponifiable Substances.**—From 6 to 8 grams of the total fat, extracted as in 3, are dissolved in about 50 c.c. of 96% alcohol and the liquid neutralised with seminormal alcoholic caustic potash in presence of phenolphthalein (to a faint pink coloration) ; it is then diluted with about 50 c.c. of water and extracted successively with 100 c.c., 50 c.c., and 50 c.c. of petroleum ether (b.pt. not above 65°). The united petroleum ether solutions are washed three times with three quantities of 10-20 c.c. of 58% alcohol and then evaporated, the residue being dried at 100-105° and weighed.

This gives the neutral fat plus any unsaponifiable substances contained in the soap.

In presence of the latter (which may be detected by a separate test), the weighed residue must be saponified with alcoholic potash, the solution extracted with petroleum ether in the manner described above, and the new extract, representing the unsaponifiable substances, weighed. The neutral fat is then given by difference.

**9. Resin.**—The presence of resin (colophony) in a soap is readily detected by the application of Morawski's reaction (*see* p. 390) to the fatty acids obtained from the soap itself, provided the latter does not contain wool fat, in which case the test is made on the fatty acids after elimination of the unsaponifiable matter.

The quantitative determination of the resin is effected by Twitchell's method (*see* p. 390)

**10. Glycerine.**—This occurs in "cold" soaps and in soft or potash soaps (3-5%), in which its presence is due to the method of preparation, and also in transparent or glycerine soaps, to which it is purposely added.

For its determination, 20-25 grams of the soap are dissolved in hot water, decomposed by means of dilute sulphuric acid and filtered to remove the fatty acids. The filtrate is neutralised, defecated with lead acetate, made up to a definite volume and filtered, the glycerine being estimated in an aliquot part by the dichromate method (*see* Glycerine).

If the soap contains ethereal oils, sugar, dextrin or other substance oxidisable by dichromate, this method is inapplicable. In such cases the defecated aqueous liquid is evaporated with addition of lime and the glycerine then extracted with alcohol and ether in the manner described for the determination of glycerine in wine.

**11. Nature of the Constituent Fats.**—The external characters of soaps give some indication of the nature of the fatty matters used in the manufacture. White and mottled soaps are mostly prepared from tallow

[1] *See* last part of preceding foot-note.

and olive, arachis, sesamé, cottonseed and coco-nut oils; yellow soaps may contain resin and palm oil, and green or brown ones, sulphocarbon oil and resin. Further, the solidifying point, acid and iodine numbers and certain colour reactions and other investigations of the fatty acids obtained from a soap give information, up to a certain point, of the character of the fats used.

For example: Soaps prepared from oleine give fatty acids which solidify at a low temperature and contain only small quantities of solid acids (for examination of these, *see* p. 384).

Soaps from coco-nut oil give fatty acids with an acid number above 205 and a low iodine number.

Those from linseed and other drying oils contain hydroxy-acids insoluble in the cold in petroleum ether and yield fatty acids with a high iodine number.

Soaps from cottonseed, sesamé and arachis oils give fatty acids which show Milliau's and Villavecchia and Fabris' reactions and contain arachidic acid (*see* Cottonseed, Sesamé and Arachis Oils, preceding chapter).

Resin soaps give the reaction for resin with acetic anhydride and sulphuric acid (*see* 9).

Tests for cholesterol and phytosterol (*see* Hog's Fat) show whether a soap contains animal or vegetable fats.

**12. Extraneous Substances.**—These may be of varied character and principally as follows:

(*a*) MINERAL SUBSTANCES. Alkaline chlorides, sulphates, carbonates and phosphates, water glass, borax, heavy spar, kaolin, talc, siliceous sand, pumice, tripoli, etc. Some soaps (especially powdered) contain also oxidising agents, such as sodium peroxide, perborates, percarbonates and persulphates.

All these substances may be recognised and determined by treating the soap with absolute alcohol and examining the insoluble residue by the ordinary analytical methods, both qualitative and quantitative.

(*b*) VARIOUS ORGANIC SUBSTANCES. These may consist of starch, flour, dextrin, sugars (saccharose, glucose, molasses), vegetable gum, albumin and casein. Such substances also remain undissolved when the soap is treated with absolute alcohol and may be detected in the residue by means of the microscope, by treating with iodine (starch, dextrin), by the rotatory and reducing powers (sugars), by the way in which they burn (proteins, etc.).

(*c*) ALCOHOL. About 50 grams of the soap are dissolved in 100 c.c. of tepid water and decomposed with a slight excess of dilute sulphuric acid and filtered. The filtrate (which should not be much more than 150 c.c.) is neutralised with potash and distilled, 100 c.c. of distillate being collected. From the density of this the alcohol is calculated.

(*d*) PERFUMES. These consist of various essential oils or of nitrobenzene (mirbane oil). To detect them, 30–50 grams of the soap are dissolved in a little water, decomposed with a slight excess of dilute sulphuric acid and distilled in a current of steam, the distillate being collected in a very narrow cylinder.

The volatile oil collects in drops or in a thin layer at the surface of the

distilled water. Ether is then added and the whole transferred to a small separating funnel, the cylinder being rinsed out with ether. After shaking, the water is withdrawn and the ethereal solution allowed to evaporate at the ordinary temperature in a small dish ; this yields the volatile oil, which may be identified by its odour and, if in sufficient quantity, by other characters

To identify nitrobenzene, the ethereal extract obtained in the above manner is dissolved in a little alcohol and a scrap of zinc and 2–3 c.c. of dilute sulphuric acid added to the solution. After 2–3 hours the liquid is filtered into a dish and the filtrate exposed for an instant to chlorine issuing from a test-tube containing a little potassium chlorate and conc. hydrochloric acid : a persistent violet coloration is produced (*Armani and Barboni*).

Soaps based on coco-nut or palm oil give, with steam, a small quantity of volatile acids of peculiar odour, which must not be confused with that of soap containing added perfume.

(*e*) MEDICINAL SUBSTANCES. Medicinal soaps are made with the most varied substances, mostly antiseptics, among which are formalin, phenol, naphthalene, tar, ichthyol, camphor, sulphur, salicylic and boric acids, mercury salts, arsenical compounds, juices of medicinal herbs, etc.

These may be tested for by shaking the soap with ether, evaporating the ethereal solution and examining the residue by suitable methods, or by dissolving the soap in water, precipitating with barium chloride and washing the barium soap thus formed with alcohol or ether.

Mercury and arsenic compounds, boric acid and the like may be detected by decomposing the soap with hydrochloric or nitric acid and then testing the acid aqueous liquid.

One of the commonest medicinal soaps contains carbolic acid. To determine the proportion of the phenol, 5–10 grams of the soap are dissolved in water with addition of caustic soda, the solution shaken with ether and the aqueous liquid treated with excess of sodium chloride to precipitate the whole of the soap. The liquid is then filtered and the insoluble residue washed with saturated sodium chloride solution, the liquid being then acidified with dilute sulphuric acid and the phenol estimated by means of bromine (*see* Carbolic Acid, p. 330).

(*f*) MINERAL AND RESIN OILS, PARAFFIN WAX, TURPENTINE, ETC. These may be detected by extraction of the soap with ether. In most cases, mixtures of soap with mineral or resin oils, vaseline and the like, constitute lubricants or cart-grease, analysis of which is dealt with in the article on Lubricants (*see* p. 365).

## GLYCERINE

*Crude glycerine* (*saponification, soap-lye* or *distillation glycerine*) forms a yellowish or brown liquid with a repellent odour and an acrid taste, while *purified glycerine* (*refined, distilled* or *double distilled, for dynamite*) consists of a colourless or almost colourless, odourless, syrupy liquid with a sweet taste.

Analysis of commercial glycerines includes qualitative tests to ascertain

the purity, and various quantitative determinations to decide its commercial value or its fitness for definite purposes.

## *A.* Crude Glycerine

Glycerine liquors from soap-works, either as they are or after concentration (as usually sold) are highly contaminated with various mineral salts (chlorides, sulphates, sulphides, sulphites, thiosulphates, lime, alkali) and organic substances (soaps, tarry substances, proteins, etc.). Their analysis is usually restricted to determinations of the alkali (free and combined), free acid, residue on evaporation, water and glycerine.[1]

**Sampling.**—The sample should contain portions from every vessel forming the parcel and should be taken, if possible, as soon as these are filled, since crude glycerine often contains suspended matters which are gradually deposited.

If such deposition has already occurred, a good average sample may be obtained with the help of a special sampler.[2]

Note is made of any suspended matter observed while the sample is being taken, and also of the temperature and of the form and capacity of the vessels when these are not similar.

**1. Ash and Total Alkali.**—From 2 to 5 grams of the glycerine are weighed in a platinum dish and evaporated carefully over a direct flame and the residue charred at the lowest possible temperature.

The carbonaceous mass is then extracted with boiling water, filtered and washed. The filter and the contained charred mass are incinerated in the same dish, the aqueous extract and wash-waters being added and the whole evaporated to dryness on a water-bath and again ignited carefully so that the ash does not fuse.

The ash thus obtained is weighed and then dissolved in water and titrated with normal acid (indicator : methyl orange), the alkalinity being expressed as percentage of $Na_2O$ in the glycerine.

**2. Free Caustic Alkali.**—20 grams of the glycerine are weighed in a 100 c.c. flask, dissolved in 50 c.c. of recently boiled water, treated with excess of barium chloride solution and 1 c.c. of alcoholic phenolphthalein solution, made up to volume with boiled water, shaken vigorously and left at rest. Subsequently 50 c.c. of the clear liquid are pipetted off and titrated with normal acid. The free alkali is calculated as $Na_2O$ per 100 parts of glycerine.

**3. Alkali as Carbonate.**—10 grams of the sample are diluted with 50 c.c. of distilled water, treated with sufficient normal acid to neutralise the total alkali (*see* 1) and boiled in a reflux apparatus for 15-20 minutes. The condenser is washed down with recently boiled distilled water and the free acid titrated with normal soda in presence of phenolphthalein.

The result is calculated as percentage of $Na_2O$ and from this is deducted

[1] The methods were fixed in 1911 by an International Commission of American, English, German and French analysts, as a result of the Congress of Glycerine manufacturers held in London in 1909.

[2] Described in *Zeitschr. angew. chem.*, 1911, I, p. 865, and *L'Industria chimica*, 1911, p. 245.

the free caustic alkali (*see* 2), the remainder being the percentage of $Na_2O$ as carbonate.

**4. Alkali combined with Organic Acids.**—The percentage of $Na_2O$ existing as organic salts is calculated by subtracting from the total $Na_2O$ (1) the sum of the free $Na_2O$ (2) and the carbonated $Na_2O$ (3).

**5. Acidity.**—Ten grams of the sample, dissolved in 50 c.c. of recently boiled water, are titrated with normal caustic soda in presence of phenolphthalein. The result is expressed as $Na_2O$ necessary to neutralise the acidity of 100 grams of the glycerine.

**6. Residue at 160°.**—In a 100 c.c. measuring flask, 10 grams of the glycerine are weighed, diluted with a little water and treated with normal acid or alkali (according as the sample is alkaline or acid) in such amount that the glycerine assumes an alkalinity corresponding with 0·2% of $Na_2O$. The liquid is then made up to volume and shaken, 10 c.c. (or, if the sample is very impure, a lesser quantity sufficient to give a residue not exceeding 30–40 milligrams) being transferred to a tared porcelain dish 12 mm. deep and with a flat base 6 cm. in diameter. The bulk of the water is evaporated off on the water-bath and the dish then placed in an air-oven (30 × 30 × 30 cm.), which is furnished with a thermometer, rests on an iron plate 20 mm. thick, and has half-way up a shelf covered with asbestos board on which the capsule containing the glycerine rests. The latter is heated at 160° until only traces of thin vapour are emitted, then removed from the oven, allowed to cool, 0·5–1 c.c. of water added and the contents gently mixed. The liquid is again evaporated on the water-bath and subsequently on the oven at 160° until the residue, placed within the oven, no longer froths. This operation usually requires 2–3 hours.

At this point the dish is kept in the oven at 160° for exactly one hour, and is then removed, allowed to cool in a desiccator over sulphuric acid and weighed. The residue is next treated with water, re-evaporated, dried, kept at 160° for an hour as before, this procedure being repeated until the loss occasioned does not exceed 1–1·5 mgrms. per hour.

The weight of the residue at 160° is *corrected* for the acid or alkali added to bring the alkalinity to the desired point. With acid glycerine, 0·022 gram is subtracted for each c.c. of normal alkali added. With alkaline glycerine, the correction applied is that resulting from the transformation of NaOH and $Na_2CO_3$ into NaCl. The corrected weight gives the residue at 160° and is calculated for 100 grams of the glycerine.

The residue is kept for the determination of any impurities capable of acetylation.

**7. Organic Residue.**—The organic residue represents the difference between the residue at 160° and the ash.

It should, however, be noted that the $CO_2$ formed for the transformation of organic acids during the incineration is not contained in the organic residue.

**8. Water.**—On a clock-glass of about 15 c.c. capacity are placed 2–3 grams of very voluminous asbestos, previously well washed with acid and then with water and dried at 100°. The whole is then left in a vacuum desiccator over sulphuric acid at a pressure of 1–2 mm. of mercury until

of constant weight. From 1 to 1·5 gram of the glycerine is then dropped on to the asbestos so that it is uniformly distributed ; after being weighed again, the glass is left in the desiccator at the above pressure until the weight is constant (usually about 48 hours at 15° are required). The loss of weight represents water.

**9. Glycerine.**—Either of two methods may be used [1] :

*A*. ACETYLATION METHOD, applicable to crude glycerine, provided it contains not more than 50% of water.

*Reagents* required :

(a) *Acetic anhydride* (puriss.), which should be carefully examined as to purity and which in a blank esterification experiment should not require more than 0·1–0·2 c.c. of normal soda, and which should turn only slightly brown when boiled for an hour with sodium acetate.

(b) *Pure dry sodium acetate*, obtained by fusing the salt in a platinum dish, powdering it rapidly and storing in a closed vessel in a desiccator. It should be absolutely free from moisture.

(c) *Normal caustic soda solution*, which should be very carefully prepared with well-boiled water and should be quite free from carbonate.

(d) *Normal sulphuric acid*.

(e) *Phenolphthalein solution*, containing 0·5 part in 100 parts of alcohol and neutralised.

*Procedure*. In a round-bottomed flask of about 120 c.c. capacity, well washed and dried, 1·25–1·50 gram of the glycerine is rapidly weighed, 3 grams of the sodium acetate and 7·5 c.c. of acetic anhydride being added. The flask is then connected with a small reflux condenser by means of a ground joint or a rubber stopper (the latter should be first purified by exposure to the vapour of boiling acetic anhydride) and the liquid boiled gently for about an hour. It is then cooled somewhat and 50 c.c. of recently boiled hot water (at about 80°) added by way of the condenser tube, the liquid being shaken and heated, if necessary—but not above 80°—until solution is complete (excepting for a few black flocks due to impurities). The condenser tube is washed down with a little boiled water, the flask detached and the stopper or ground joint also washed down. The liquid is filtered into a flask holding about a litre, the original flask and filter being thoroughly washed with boiled, cold water. 2 c.c. of phenolphthalein solution are next added and the liquid neutralised with the normal caustic soda solution (to a faint yellowish-red coloration), care being taken to shake the flask continually while the alkaline solution is run in from a burette.

After the neutral point is reached, a further quantity of 50 c.c. of normal caustic soda is added, the flask being then closed with a stopper traversed by a long glass tube to act as reflux condenser, and the liquid boiled gently for 15 minutes, then cooled rapidly and the excess of alkali titrated with the normal acid until the original yellowish-red tint reappears.

At the same time a check experiment is made under the same conditions.

From the quantity of caustic soda used to saponify the triacetin (difference between the volume of caustic soda added after neutralisation and the

[1] Recommended by the Committee mentioned above.

volume of acid required in the final titration), less any volume found in the check determination, the glycerine is calculated: 1 c.c. normal alkali = 0·03069 gram of glycerine.

With *crude soap-lye glycerine*, when this contains more than 2·5% of organic residue at 160° (*see* 7), the residue at 160° obtained as in 6 (above) must also be acetylated in the manner just described; if the result thus obtained corresponds with more than 0·5% of glycerine (on the residue itself), the excess over 0·5% is deducted from the percentage of glycerine found in the sample itself.

For *distilled saponification glycerine* and the like, acetylation of the organic residue is carried out when this exceeds 1%, the procedure being as before and account being taken only of the excess of glycerine over 0·5%.

*B.* DICHROMATE METHOD. *Reagents* required:

(a) *Potassium dichromate* (puriss.), powdered, dried at 110–120° and kept in a well-closed vessel.

(b) *Standard dichromate solution*: 7·4564 grams of dichromate (*a*) are dissolved in water to 1 litre.

(c) *Ferrous ammonium sulphate*, to be titrated with the dichromate as follows: 3·7282 grams of the dichromate are dissolved in 50 c.c. of water and 50 c.c. of dilute sulphuric acid (*g*). A convenient excess of ferrous ammonium sulphate (e.g., 3–4 grams), accurately weighed, is then added and the excess determined by means of the dichromate solution (*b*), a drop of the liquid being removed from time to time and tested with potassium ferricyanide. The amount of dichromate corresponding with 1 gram of pure ferrous ammonium sulphate is then calculated (with pure products 1 gram of the sulphate = 1·25 gram of the dichromate).

(d) *Silver carbonate*, to be prepared afresh for each operation by treating 140 c.c. of 0·5% silver sulphate solution with 4·9 c.c. of normal sodium carbonate solution, allowing the precipitate to deposit, decanting off the liquid and washing once by decantation.

(e) *Basic lead acetate*, obtained by boiling 10% neutral lead acetate solution with excess of litharge for an hour and filtering while hot.

(f) *Potassium ferricyanide* in 0·1% solution.

(g) *Dilute sulphuric acid*, conc. acid being mixed with its own volume of water.

*Procedure.* 20 grams of the sample are made up to 250 c.c. with water in a 250 c.c. flask. Of this solution, 25 c.c. are treated, in a 100 c.c. flask, with the silver carbonate (*d*) and, after about 10 minutes, with 5 c.c. of the lead acetate (*e*), the liquid being then made up to the mark and 1·5 c.c. of extra water added to compensate for the volume of the precipitate. The whole is then shaken vigorously and filtered through a dry filter, the first 10 c.c. of filtrate being discarded and the remainder refiltered if turbid.[1] A small portion is tested to ascertain if fresh addition of the lead acetate gives a further precipitate: if this is the case, the above treatment is repeated with a fresh volume of 25 c.c. of the original solution but with 6 c.c. of the lead acetate; this is, however, seldom required.

[1] To obtain a clear filtrate, a few c.c. of 10% sodium sulphate solution may be added before the liquid is made up to volume.

25 c.c. of the filtrate are treated in a clean beaker (washed w dichromate and sulphuric acid) with 12 drops of dilute sulphuric a (1 : 4) to precipitate the excess of lead and then with 3·7282 grams of t powdered dichromate (*a*) and 25 c.c. of water. When the dichromate dissolved, 50 c.c. of the dilute sulphuric acid (*g*) are added and the beal kept in a boiling water-bath for two hours, care being taken to protect from organic vapours (alcohol, etc.) and from dust. It is then allowed cool, an exactly weighed amount (in excess) of ferrous ammonium sulph (e.g., 3-4 grams) being added and the extent of the excess measured titration with the dichromate solution (*b*), potassium ferrocyanide bei used, as before, as indicator.

As it is known from the titration of the ferrous ammonium sulph (*see c*) with how much dichromate 1 gram of the ferrous salt correspon the quantity of dichromate used in oxidising the glycerine, and from t the amount of the glycerine, may be calculated : 1 gram of the dichrom = 0·13411 gram of glycerine.

As regards these two methods, adopted by the International Commissi Tortelli and Ceccherelli [1] point out that only the second—the dichromate met —is really exact. The acetin method, according to the accurate investigati of these authors, gives inconstant and low results.

The same authors also suggest some practical modifications in the dichrom method.

## *B.* Pure Glycerine

With pure glycerines the specific gravity is determined and varic common impurities (heavy metals, sulphates, chlorides, oxalates, lir arsenic, acrolein, formic acid, fats) and adulterations (sugar, dextr tested for. In some cases the chlorides are determined and possibly t residue at 160° and other determinations described for crude glyceri With dynamite glycerine, a nitration test is made.

**1. Specific Gravity.**—This is determined by the Westphal balan picnometer or hydrometer.

If the glycerine is pure, the content of water may be calculated fr the specific gravity by means of the following table (page 469).

**2. Detection of Impurities and Adulterations.**—This is effect by means of the following tests :

(*a*) 1 volume of the glycerine is dissolved in 5 vols. of water and t reaction of the solution tested with litmus paper : pure glycer[illegible] shou be neutral.

Aliquot parts of the same solution are then treated with hydr[illegible] sulphide and with ammonium sulphide to ascertain if *heavy metals* present (brown coloration) ; with barium chloride for the detection *sulphates*, with silver nitrate for that of *chlorides*, with calcium chloride that of *oxalates* and with ammonium oxalate for that of *calcium salts*.

(*b*) 1 c.c. of the glycerine is treated with 5 c.c. of Bettendorf's reage for the detection of *arsenic* : no coloration should be detectable within hour.

[1] *Annali di chimica applicata*, 1914, I, p. 514.

TABLES LI

## Specific Gravity of Aqueous Glycerine

| Specific gravity according to | | Percentage by weight of Glycerine. | Specific gravity according to | | Percentage by weight of Glycerine. |
|---|---|---|---|---|---|
| Lenz at 12–14° Water at 12°=1 | Gerlach at 15° Water at 15°=1 | | Lenz at 12–14° Water at 12°=1 | Gerlach at 15° Water at 15°=1 | |
| 1·2691 | 1·2653 | 100 | 1·2212 | 1·2184 | 82 |
| 1·2664 | 1·2628 | 99 | 1·2185 | 1·2157 | 81 |
| 1·2637 | 1·2602 | 98 | 1·2159 | 1·2130 | 80 |
| 1·2610 | 1·2577 | 97 | 1·2016 | 1·1990 | 75 |
| 1·2584 | 1·2552 | 96 | 1·1889 | 1·1850 | 70 |
| 1·2557 | 1·2526 | 95 | 1·1733 | 1·1711 | 65 |
| 1·2531 | 1·2501 | 94 | 1·1582 | 1·1570 | 60 |
| 1·2504 | 1·2476 | 93 | 1·1455 | 1·1430 | 55 |
| 1·2478 | 1·2451 | 92 | 1·1320 | 1·1290 | 50 |
| 1·2451 | 1·2425 | 91 | 1·1183 | 1·1155 | 45 |
| 1·2425 | 1·2400 | 90 | 1·1045 | 1·1020 | 40 |
| 1·2398 | 1·2373 | 89 | 1·0907 | 1·0885 | 35 |
| 1·2372 | 1·2346 | 88 | 1·0771 | 1·0750 | 30 |
| 1·2345 | 1·2319 | 87 | 1·0635 | 1·0620 | 25 |
| 1·2318 | 1·2292 | 86 | 1·0498 | 1·0490 | 20 |
| 1·2292 | 1·2265 | 85 | 1·0374 | — | 15 |
| 1·2265 | 1·2238 | 84 | 1·0245 | 1·0245 | 10 |
| 1·2238 | 1·2211 | 83 | 1·0123 | — | 5 |

(*c*) 1 c.c. of the glycerine and 1 c.c. of ammonia are heated to 60° and 3 drops of silver nitrate solution then added: the appearance of a brown coloration or deposit within 5 minutes denotes the presence of *acrolein* or *formic acid*.

(*d*) 1 c.c. is heated with 1 c.c. of 15% sodium hydroxide solution: evolution of ammonia indicates the presence of *ammonium* salts, or yellowing of the solution the presence of *glucose*. The presence of the latter may be confirmed by boiling a few drops of the glycerine with Fehling's solution (red precipitate).

(*e*) 1 c.c. is heated gently with dilute sulphuric acid to ascertain if an unpleasant rancid odour is evolved (*fatty substances*); the liquid is then neutralised and boiled with Fehling's solution (*sugar*).

(*f*) 1 volume of the glycerine is treated with about 2 vols. of strong alcohol: turbidity denotes presence of *gum* or *dextrin*.

(*g*) A few c.c. of the glycerine are evaporated in a small dish to ascertain if any residue remains (usually *mineral substances*).

**3. Chlorides.**—A known weight of the glycerine is carefully burnt, the residue charred at a low temperature and lixiviated with water and the chlorine in the solution determined volumetrically. The result is expressed as sodium chloride.

**4. Nitration Test** (for dynamite glycerine).—Into a very wide beaker, 150 grams of nitrating mixture (1 part by weight of nitric acid of D = 1·5

and 2 parts by weight of sulphuric acid of D = 1·845) are poured and on to this are carefully dropped 20 grams of the glycerine, the beaker being externally cooled with water meanwhile.' The product is subsequently transferred, with every precaution, to a graduated cylinder and note taken if the nitroglycerine separates promptly and if it is pale and clear. When the separation of the nitroglycerine from the acid liquid is sharp, the volume of the former is measured ; multiplication of this volume by 1·609 (specific gravity of nitroglycerine at 15°) gives the weight.

***

*Glycerine liquors* obtained directly by saponification with alkali or in an autoclave contain 5–10% of glycerine, whereas those resulting from saponification by Twitchell's method or by enzymes contain 12–19%.

*Crude glycerine* (concentrated) usually contains 80–90% of glycerine and varying quantities of salts (ash), residue fixed at 160°, free acids or alkalies, etc.

*Refined glycerine* (pure, puriss.) should be free or almost so from the different impurities already mentioned (*see* Pure Glycerine, 2).

Double distilled glycerine for pharmaceutical purposes should, in particular, satisfy the various tests indicated under 2.

*Dynamite glycerine* should have a specific gravity not less than 1·261, should be perfectly neutral, should contain no more than traces of chlorides (not more than 0·025% of NaCl), sulphates, lime, magnesia, alumina and reducing substances, and not more than 0·25% of residue fixed at 160°. In the nitration test it should give not less than 200% of nitroglycerine (theoretical yield, 246·7%), which should separate promptly as a colourless or almost colourless, perfectly clear liquid.

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